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# UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 C.F.R. § 1.53(b))

| | |
|---|---|
| Attorney Docket No. | |
| First Inventor or Application Identifier | Savvas Vasileiadis |
| Title | Permreactor and separator type fuel processors for production of hydrogen and hydrogen-carbon oxides mixtures |
| Express Mail Label No. | |

## APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

ADDRESS TO: Assistant Commissioner for Patents, Box Patent Application, Washington, DC 20231

1. [X] * Fee Transmittal Form (e.g., PTO/SB/17) (Submit an original and a duplicate for fee processing)
2. [X] Specification [Total Pages 44] (preferred arrangement set forth below)
   - Descriptive title of the Invention
   - Cross References to Related Applications
   - Statement Regarding Fed sponsored R & D
   - Reference to Microfiche Appendix
   - Background of the Invention
   - Brief Summary of the Invention
   - Brief Description of the Drawings (if filed)
   - Detailed Description
   - Claim(s)
   - Abstract of the Disclosure
3. [X] Drawing(s) (35 U.S.C. 113) [Total Sheets 13]
4. Oath or Declaration [Total Pages ]
   a. [X] Newly executed (original or copy)
   b. [X] Copy from a prior application (37 C.F.R. § 1.63(d)) (for continuation/divisional with Box 16 completed) (Abstract)
      i. [ ] DELETION OF INVENTOR(S) Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).

* NOTE FOR ITEMS 1 & 13: IN ORDER TO BE ENTITLED TO PAY SMALL ENTITY FEES, A SMALL ENTITY STATEMENT IS REQUIRED (37 C.F.R. § 1.27), EXCEPT IF ONE FILED IN A PRIOR APPLICATION IS RELIED UPON (37 C.F.R. § 1.28).

5. [ ] Microfiche Computer Program (Appendix)
6. Nucleotide and/or Amino Acid Sequence Submission (if applicable, all necessary)
   a. [ ] Computer Readable Copy
   b. [ ] Paper Copy (identical to computer copy)
   c. [ ] Statement verifying identity of above copies

## ACCOMPANYING APPLICATION PARTS

7. [ ] Assignment Papers (cover sheet & document(s))
8. [ ] 37 C.F.R.§3.73(b) Statement (when there is an assignee) [ ] Power of Attorney
9. [ ] English Translation Document (if applicable)
10. [X] Information Disclosure Statement (IDS)/PTO-1449 [X] Copies of IDS Citations
11. [ ] Preliminary Amendment
12. [X] Return Receipt Postcard (MPEP 503) (Should be specifically itemized)
13. [X] * Small Entity Statement(s) (PTO/SB/09-12) [ ] Statement filed in prior application, Status still proper and desired
14. [ ] Certified Copy of Priority Document(s) (if foreign priority is claimed)
15. [ ] Other: ...............

16. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment:
[ ] Continuation [ ] Divisional [X] Continuation-in-part (CIP) of prior application No: 08/595,040
Prior application information: Examiner Sreeni Padmanabhan Group / Art Unit: 1621

**For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 4b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.**

## 17. CORRESPONDENCE ADDRESS

[ ] Customer Number or Bar Code Label (Insert Customer No. or Attach bar code label here) or [X] Correspondence address below


| | | | | | |
|---|---|---|---|---|---|
| Name | Savvas Vasileiadis<br>ZivaTech | | | | |
| Address | 15549 Dearborn Street | | | | |
| City | North Hills | State | CA | Zip Code | 91343-3267 |
| Country | USA | Telephone | 818-8934292 | Fax | 818-8934292 |


| | | | |
|---|---|---|---|
| Name (Print/Type) | Savvas Vasileiadis | Registration No (Attorney/Agent) | |
| Signature | Vasileiadis | Date | 3/7/2000 |

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## STATEMENT CLAIMING SMALL ENTITY STATUS (37 CFR 1.9(f) & 1.27(c))--SMALL BUSINESS CONCERN

Docket Number (Optional)

Applicant, Patentee, or Identifier: Savvas Vasileiadis
Application or Patent No.:
Filed or Issued: 3/7/2000
Title: "Permreactor and Separator type fuel processors for production of hydrogen and hydrogen, carbon oxides mixtures".

I hereby state that I am
- [x] the owner of the small business concern identified below:
- [ ] an official of the small business concern empowered to act on behalf of the concern identified below:

NAME OF SMALL BUSINESS CONCERN ZiVaTech

ADDRESS OF SMALL BUSINESS CONCERN 15549 Dearborn street, North Hills, CA 91343, USA

I hereby state that the above identified small business concern qualifies as a small business concern as defined in 13 CFR Part 121 for purposes of paying reduced fees to the United States Patent and Trademark Office. Questions related to size standards for a small business concern may be directed to: Small Business Administration, Size Standards Staff, 409 Third Street, SW, Washington, DC 20416.

I hereby state that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention described in:

- [x] the specification filed herewith with title as listed above.
- [x] the application identified above.
- [x] the patent identified above.

If the rights held by the above identified small business concern are not exclusive, each individual, concern, or organization having rights in the invention must file separate statements as to their status as small entities, and no rights to the invention are held by any person, other than the inventor, who would not qualify as an independent inventor under 37 CFR 1.9(c) if that person made the invention, or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d), or a nonprofit organization under 37 CFR 1.9(e).

Each person, concern, or organization having any rights in the invention is listed below:
- [x] no such person, concern, or organization exists.
- [ ] each such person, concern, or organization is listed below.

Separate statements are required from each named person, concern or organization having rights to the invention stating their status as small entities. (37 CFR 1.27)

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

NAME OF PERSON SIGNING Savvas Vasileiadis

TITLE OF PERSON IF OTHER THAN OWNER

ADDRESS OF PERSON SIGNING 15549 Dearborn street, North Hills, CA 91343

SIGNATURE SVasileiadis DATE 3/7/2000

**Prior Application Number: 08/595,040**

**TITLE**

REACTOR-MEMBRANE PERMEATOR PROCESS FOR HYDROCARBON REFORMING AND WATER GAS SHIFT REACTIONS

**Inventors**

Zoe Ziaka and Savvas Vasileiadis
15549 Dearborn street, North Hills CA 91343, USA

**ABSTRACT**

New process designs are presented for reforming reactions of steam with hydrocarbons (such as methane, natural gas, light hydrocarbon feedstocks with one to four carbon atoms in each molecule), also for the water gas shift reaction that is of steam with carbon monoxide; also for carbon dioxide reforming of hydrocarbons (such as methane, acidic natural gas, coal gas, landfill gas, light hydrocarbon feedstocks with one to four carbon atoms in each molecule), and the combined reaction of steam carbon dioxide with same hydrocarbons. The processes employ organic polymer, organic polymer-inorganic support, and inorganic membrane permeators for species separation, with the permeators placed after the reactors where the above named reactions take place. The membranes in permeators separate selectively the $H_2$ and $CO_2$ species exiting from the reactors from the non-permeated reactants and products. The reject streams coming out of permeators can be recycled into the inlet of the first reactors; these reject streams can be also fed to consecutively placed steam reforming and water gas shift reactors for further conversion to $H_2$ and $CO_2$ products. The separated $H_2$ and $CO_2$ in membrane permeate and from the secondary reactions of permeator reject streams, can be used for direct methanol synthesis, feed to molten carbonate fuel cells, and other chemical syntheses; after the removal of $CO_2$ from the mixture, pure hydrogen can be recovered and used in chemical syntheses and as fuel in fuel cells and power generation cycles.

# SPECIFICATION

Total pages: 44

Total claims: 45

**PERMREACTOR AND SEPARATOR TYPE FUEL PROCESSORS FOR PRODUCTION OF HYDROGEN AND HYDROGEN, CARBON OXIDES MIXTURES**

Savvas Vasileiadis and Zoe Ziaka-Vasileiadou
ZiVaTech, 15549 Dearborn street, North Hills CA 91343, USA

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## TECHNICAL FIELD

This invention relates to new process and reactor designs including permeable reactors (permreactors) and permeators for the hydrocarbon steam reforming, hydrocarbon carbon dioxide reforming, combined hydrocarbon steam and carbon dioxide reforming, alcohol steam reforming, water gas shift, paraffin dehydrogenation, methanol synthesis, and combination of these conversion reactions for production of valuable fuels and chemicals. It also relates to the utilization of the end reaction products such as pure hydrogen, hydrogen and carbon monoxide, hydrogen and carbon dioxide, and mixtures of these species, into specific applications such as fuel cells, gas turbines, gas engines and synthesis reactors.

## BACKGROUND OF THE INVENTION

This current application is continuation in part of the application # 08/595040 filed 1/31/1996.

This current invention describes new and improved process and reactor designs which involve permeable reactors (permreactors) and permeators for the hydrocarbon steam reforming, hydrocarbon carbon dioxide reforming, combined hydrocarbon steam and carbon dioxide reforming, alcohol steam reforming, the water gas shift reaction, dehydrogenation reactions of hydrocarbons, such as dehydrogenation of alkanes (i.e., paraffins) to alkenes, and combination of these previous reactions.

The reactions and heats of reactions that are referred to and utilized within the embodiments of the invention are well known and are listed below:

$CH_4 + H_2O = CO + 3H_2$ ($\Delta H^o_{298}$=206.1kJ/mol), methane-steam reforming (1)

$CH_4 + CO_2 = 2CO + 2H_2$ ($\Delta H^o_{298}$=247.3kJ/mol), methane-$CO_2$ reforming (2)

$CO + H_2O = CO_2 + H_2$ ($\Delta H^o_{298}$=-41.15kJ/mol), water gas shift (3)

$C_nH_{2n+2}=C_nH_{2n} + H_2$ (endothermic dehydrogenation reactions, heat of reaction varies depending on the type of feedstock processed in the reactor, e.g., ethane, propane, butane, pentane) (4)

$CO + 2H_2 = CH_3OH$ ($\Delta H^o_{298}$=-128.2kJ/mol), methanol synthesis (5)

$CO_2 + 3H_2 = CH_3OH + H_2O$ ($\Delta H^o_{298}$=-49.5kJ/mol), methanol synthesis (6)

$CH_3OH + H_2O = CO_2 + 3H_2$ ($\Delta H^o_{298}$= 49.5kJ/mol), methanol-steam reforming (7)

These are catalytic reactions utilizing catalysts such as nickel (Ni), ruthenium (Ru), rhodium (Rh), palladium (Pd), platinum (Pt), chromium (Cr), copper (Cu), zinc (Zn), Cobalt (Co), Gold (Au) and other metals, and bimetallic catalyst compositions of these metals. The catalysts are supported on alumina ($Al_2O_3$), titania ($TiO_2$), silica ($SiO_2$), zirconia ($ZrO_2$), lanthanum ($La_2O_3$) and other supports, enriched with earth metals such as Ca, La, Na, K.

Use of reactor and membrane permeator configurations and systems disclosed in our previous US patent application: # 08/595040, increase the overall process efficacy by increasing the total conversion of the following feedstocks: hydrocarbon, hydocarbon-$CO_2$ mixtures, methane, methane-$CO_2$ mixtures, alcohols. Moreover, the yields to hydrogen and carbon monoxide or hydrogen and carbon dioxide are increased by the use of the integrated membrane permeators which separates effectively $H_2$ and $CO_2$ gases. Process efficiency is further improved by the recycling of unreacted and non-separated (non-permeated) hydrocarbon (e.g., methane) and carbon monoxide into the first (primary) reactor (reformer) or the alternative direction of the same stream into a consecutive catalytic reactor (reformer or water gas shift reactor) for additional production of hydrogen and carbon dioxide. Direct utilization of the produced and separated hydrogen, synthesis gas, and hydrogen-carbon dioxide mixtures from these processes into consecutive synthesis reactors, fuel cells and gas turbines and engines are additional advantages and continual applications of the proposed processes.

Current invention elaborates on the substitution of the primary conventional reactor (i.e., reformer, water gas shift, dehydrogenation reactor) by a permeable (membrane-type) reactor (so called permreactor for simplicity) of specific design, and the correspondingly derived improved process and permeable reactor-separator configurations for the above mentioned reactions. Moreover, introduction and specification of double wall permreactors, besides the single wall permreactors, for conducting similar reactions are also disclosed. The described permreactors are designed to consist of interconnected parts which can be readily taken apart and assembled when service is necessary. For the disclosed integrated reaction-separation systems specific applications are disclosed such as the utilization of the end products and/or permeated (separated) streams into consecutively placed synthesis reactors (including additional reformers or water gas shift reactors), gas turbines and engines, and various types of hydrogen based fuel cells and related fuel cell systems.

Previous reactor and permeable reactor designs from the above cited references refer mainly to methane and methanol steam reforming reactions but not to carbon dioxide reforming, water gas shift and dehydrogenation reactions as the present invention does. Moreover, previous inventions refer to a single reactor or permreactor or other reaction vessel instead of reactor-separator systems as the present invention describes. Present invention introduces double permeable-wall (double membrane-wall) reactors for hydrocarbon and alcohol processing reactions. The double membrane-wall reactors can be of various designs as disclosed within the embodiments of the invention. These can be catalytic reactors as adapted to specific process requirements in terms of setting key operating variables such as reaction temperature, pressure, space velocity, feed composition, to deliver final products (i.e., hydrogen and synthesis gas) in the purity and

throughput required by consecutive applications. Moreover, flexibility in the selection of permreactor wall materials such as metals, inorganics, organics and composites, allows design of multifunctional permeable reactors which separate and deliver specific species (e.g., gases) with the required purity and throughput to consecutive applications. Flexibility in the selection of functional and specific permreactor wall materials for each process operation have also economic advantages. Current disclosed permreactor, separator, and overall process designs can utilize membrane materials selected from classes of metals, inorganics (non-porous or porous), polymers, carbons and carbonaceous materials, and composites. Therefore, the selection of less expensive membrane materials for a specific permreactor, permeator and process operation is available with current invented designs.

Present invention also teaches direct utilization of end product streams to consecutive synthesis reactors, fuel cells, gas turbines and gas engines. Present invention focuses on converting and upgrading primary hydrocarbon feedstocks such as methane, natural gas, coal gas, refinery feedstocks such as naphtha and alcohol feedstocks such as methanol and ethanol to higher calorific value hydrogen and carbon oxide mixtures; also it focuses on converting secondary and waste hydrocarbon feedstocks such as acidic natural gas, biomass gas to same valuable end products. Therefore, present invention describes environmentally benign reactor designs and process designs which abate and upgrade at the same time otherwise waste gases to valuable hydrogen, synthesis gas, hydrogen and carbon dioxide mixture. In situ conversion of carbon dioxide containing hydrocarbon mixtures and abatement of the carbon dioxide negative atmospheric and terrestrial greenhouse effect can be considered an additional benefit from the implementation of the invention.

## SUMMARY OF THE INVENTION

The present invention discloses double wall permeable reactors and the related elaborate reactor designs, which offer operational advantages by conducting in-situ reactions, in comparison with single wall permeable reactors and conventional non-permeable reactors. Consequently, three different permeable reactor configurations are disclosed. These reactor designs are applied to catalytic hydrocarbon and alcohol reforming, water gas shift and hydrocarbon dehydrogenation reactions. The first design is a double wall permreactor which consists of three concentric hollow cylindrical tubes with the two inner ones to be made by permeable metal, inorganic, carbon or polymer materials depending on the type of feedstocks used and the desired composition of final exit streams. Heating tubes run through the most-inner cylinder which is also filled with the main reaction catalyst. Similarly, the second reactor design consists also of three concentric hollow cylindrical tubes with the two inner ones to be made by permeable metal, inorganic, carbon or polymer materials but with the main reaction catalyst to be contained in the annular space between the most-outer and the next-inner tubes. Heating in this design is achieved by heating the external side of the most-outer tube. Third reactor design consists of an outer impermeable tube which nests multiple organic polymer or composite polymer tubes for gas permeation. Outer tube contains also the

main reaction catalyst which is located around the polymer tubes. Heating is achieved by external heating of the outer tube. Moreover, the invention pertains to systems of the described permeable reactors with consecutive permeators for separation and further processing of post-reaction gases exiting from the reactors. Permeators can be made by polymer membranes for the concomitant separation of hydrogen and carbon dioxide gases or by metal, non-porous inorganic and carbon membranes for the separation of hydrogen only. These permreactor-permeator systems are applied to combined hydrocarbon steam and carbon dioxide reforming, hydrocarbon steam reforming, hydrocarbon carbon dioxide reforming, alcohol steam reforming, water gas shift and paraffin dehydrogenation reactions for increasing the reactant conversion and the yield to hydrogen, carbon monoxide and carbon dioxide. The separated hydrogen and carbon oxides are used in further chemical synthesis reactions and as fuel in fuel cells, gas turbines and gas engines. The invention also includes hydrocarbon-$CO_2$-steam reforming systems of permreactors with cryogenic separators wherein the consecutive permeators are replaced by cryogenic separators and pure hydrogen and carbon monoxide are recovered as final products. Similar permreactors are also directly interconnected with solid oxide fuel cells for use of the products hydrogen, carbon monoxide and steam as direct fuel in the anode of the cell. Finally, the invention includes use of the disclosed permreactors in series with methanol synthesis and methanol reforming reactors for final production of methanol, hydrogen and carbon dioxide for use as synthesis chemicals or fuels. Detailed description of the invention are presented in the embodiments of the following Figures.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1, shows the cross section of a concentric double permeable wall cylindrical reactor with tubular type heaters located along the catalyst zone, consisting of an inner metal, non-porous or porous inorganic, or carbon membrane tube and an outer membrane tube made by metal, non-porous inorganic, carbon or organic membrane enclosed within a far-outer impermeable tube.

Fig.2, shows multiple double permeable wall reactors of those described in Fig.1, but without the external impermeable tube, which are placed symmetrically inside a larger common stainless steel tube, to create a multiple tube reactor with a common external area for collecting final permeate hydrogen.

Fig.3, shows a cross section of a concentric double permeable wall cylindrical reactor, consisting of an outer impermeable tube, a next-inner membrane tube made by metal, non-porous or porous inorganic, or carbon membrane, and a most-inner membrane tube made by metal, non-porous inorganic, carbon or organic membrane.

Fig.4, shows multiple double permeable wall cylindrical reactors of those described in Fig.3, which are placed symmetrically inside a larger stainless steel tube, to create a multiple tube reactor with a common external heating area.

Fig5., shows a cross section of a multiple permeable membrane tube reactor wherein the membranes are made by an organic or composite polymer and are nested within an outer impermeable tube.

Fig.6, shows a system of a catalytic permreactor and a consecutive permeator or optionally a system of two catalytic permreactors in series for hydrocarbon steam and $CO_2$ reforming or for hydrocarbon $CO_2$ reforming only. The reject from the permeator stream containing non-permeate hydrocarbon and CO can be optionally fed into a consecutive catalytic steam reforming reactor.

Fig.7, shows a similar process as in Fig.6 in which the initial feedstock consists only of CO and steam, to undergo water gas shift reaction only in the first catalytic permreactor. The reject from the permeator, CO stream, can be recycled into the initial permreactor or optionally fed into a consecutive water gas shift reactor.

Fig.8, shows a permreactor-permeator or reactor-permeator system applied for catalytic dehydrogenation of $C_1$-$C_4$ or higher alkane hydrocarbons; the reject from the membrane permeator olefinic stream can be used for polyolefin production.

Fig.9, shows a catalytic permreactor-permeator system for the hydrocarbon steam reforming reaction. The reject from the membrane permeator hydrocarbon and CO stream can be recycled into the initial reformer or fed into a consecutive steam reforming reactor.

Fig.10, shows a system of a catalytic permreactor or impermeable reactor with a consecutive cryogenic separator for hydrocarbon steam and $CO_2$ reforming or for hydrocarbon $CO_2$ reforming only. The one stream separated from the cryogenic separator, containing hydrocarbon, $CO_2$ and steam can be alternatively fed into the inlet of the initial reforming reactor.

Fig.11, shows a system of a catalytic permreactor or impermeable reactor for hydrocarbon steam and $CO_2$ reforming or hydrocarbon $CO_2$ reforming only with complete conversion of hydrocarbon and $CO_2$ gases to $H_2$ and CO, which product mixture is fed directly into a SOFC (solid oxide fuel cell) unit for electric current generation.

Fig.12, shows a system of a catalytic permreactor or impermeable reactor followed by a membrane permeator for hydrocarbon steam and $CO_2$ reforming or hydrocarbon $CO_2$ reforming only with complete conversion of hydrocarbon and $CO_2$ feedstocks to $H_2$ and CO which product mixture enters into the permeator which separates $H_2$ via permeation from CO.

Fig.13, shows a system of a catalytic permreactor for hydrocarbon, steam and $CO_2$ reforming or hydrocarbon $CO_2$ reforming only with a consecutive methanol synthesis reactor from hydrogen, CO and $CO_2$ or hydrogen and CO only followed by a methanol steam reforming reactor for production of $H_2$ and $CO_2$. The system of reactors includes recycling streams of $H_2$ and $CO_2$ for increasing the overall process efficacy.

DETAILED DESCRIPTION OF THE DRAWINGS

Fig.1 shows a cross section of the membrane reactor to be used in steam and carbon dioxide reforming of hydrocarbons, steam reforming of alcohols, water gas shift and dehydrogenation reactions, which consists of a concentric double wall cylindrical assembly with tubular type heaters located within the catalyst, along the catalyst zone. An outer impermeable tube (7) nests the two permeable concentric tubes. Reacting

feedstocks such as steam and hydrocarbon, $CO_2$ and hydrocarbon, steam, $CO_2$ and hydrocarbon, steam and alcohols, or alkanes (paraffins) such as ethane, propane, n-butane, i-butane, pentane, naphtha and higher paraffins, are fed within the main catalyst zone (4) through special inlet fittings and they react in the catalyst to produce hydrogen, carbon monoxide, carbon dioxide. Optionally, small volumetric quantities of hydrogen can be added into above feedstocks to prevent heavy catalyst deactivation in the reactor inlet, wherein propensity for hydrocarbon cracking into carbon is high in absence of any hydrogen. The hydrocarbon reforming catalyst can be nickel, ruthenium, rhodium, palladium enriched with earth type metals such as potassium, calcium, magnesium, lanthanum, cerium, and supported on alumina, silica, titania, zirconia or other inorganic oxide. For the water gas shift reaction the catalytic metal can be nickel, also iron, copper, zinc, chromium, cobalt enriched with and supported on similar metal oxides. The methanol reforming catalysts can be zinc, chromium, copper, iron, nickel, ruthenium, rhodium, palladium. Finally, the above described reactor design is applied as well for paraffin (alkane) dehydrogenation reactions and the reactor becomes a catalytic dehydrogenator which utilizes platinum, chromium, palladium catalysts enriched with and supported on similar inorganic oxides.

Hydrogen is removed along the inner membrane tube (2), wherein the membrane is made by a metal or inorganic (non-porous or porous), porous inorganic-metal or carbon material. Carbon monoxide, carbon dioxide, steam, hydrocarbons, alcohols may also permeate through first membrane in a lesser degree than hydrogen if the membrane is porous inorganic or inorganic-metal. An inert carrier gas such as argon, nitrogen, steam or a mixture of these gases may flow along the permeate annulus, between tubes (2) and (1), through suitable inlet fittings, to carry the permeate components at a specific pressure value. Permeate hydrogen is further removed through permeation along the outer membrane tube (1) so that permeated stream contains pure hydrogen only, with pure hydrogen to be used in various applications including feed to synthesis reactors, gas turbines and engines, and fuel cells. Outer membrane tube (1) is made by a metal, non-porous inorganic or carbon membrane which allows only hydrogen to permeate through, and therefore purifies hydrogen from the permeating carbon oxides, steam and hydrocarbons, in the annular zone between the two membrane tubes.

Metal materials permeable to hydrogen for the membrane tubes (1) and (2), include palladium, vanadium, and palladium alloys such as palladium-nickel, palladium-silver, palladium-zinc, palladium-chromium, palladium-copper, palladium-tungsten and others. Hydrogen permeable non-porous inorganic membranes include silicon carbide, silicon nitride, tungsten carbide, tungsten nitride, titanium carbide, titanium nitride, tantalum carbide, tantalum nitride and others. Porous inorganic membranes include alumina, silica, titania, zirconia, various types of glass and others. Carbon type membranes are made by deposition or other fabrication method (i.e., pyrolysis) of carbon or carbonaceous materials within a porous substrate to make it hydrogen permeable.

Metal and metal alloys can be deposited on porous inorganic or metal surfaces to make them hydrogen permeable. Palladium and other metal deposition as membranes can be done with electroless plating, electroplating, sputtering, chemical vapor deposition, physical vapor deposition and other applicable metal deposition or metallization techniques. Inorganic, inorganic-metal membrane materials can be

deposited as well in porous inorganic or metal surfaces via various deposition techniques including incipient wetness, dip coating and sol gel methods.

Organic polymer, composite or copolymer membranes can be made by polymers such as polyimides, polycarbonates, polysulfones, polybenziimidazoles, polyphosphazenes, polyamides, polystyrenes, polycaprolactams, parylenes, polyvinyl halides, polyacetates, polysiloxanes and others to be permeable to hydrogen or to hydrogen and carbon dioxide. Finally, composites of the previous materials can be also made as hydrogen permeable membranes such as inorganic-metal, inorganic-organic, inorganic-metal-organic composites. Metal and metal alloy, non-porous inorganic and carbon membranes are highly selective to hydrogen, while porous inorganic, organic, and composite membranes are usually selective to other species as well. The disclosed double permeable wall reactor design can be fabricated by selecting among the aforementioned materials to satisfy process requirements for the reactor itself and the consecutive application processes disclosed later in the text.

The external space, created between the outer hydrogen permeable membrane tube (1) and the impermeable far outer shell (7), which receives the final permeate hydrogen, can be either empty, or may contain a selective catalyst (5) which converts permeate hydrogen after its combination with a component flowing in the external space parallel to the outer membrane tube. Such a flowing (sweep) component can be an unsaturated hydrocarbon (e.g., alkenes, alkynes) for conversion to saturated hydrocarbons after reaction with hydrogen, in an exothermic reaction. Flowing (sweep) component can be also carbon monoxide for direct production of methanol or gasoline (through Fischer-Tropsch synthesis) after combination with the permeate hydrogen in exothermic type reactions. Flowing gas can be nitrogen for exothermic ammonia synthesis after its combination with the permeate hydrogen. Other combination reactions of flowing species with permeate hydrogen can be these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides and these for reduction of nitroalkanes and aromatic nitro compounds to corresponding primary amines.

The heat generated by exothermic reactions in the external shell, may be transferred into the catalytic reaction zone of the inner membrane tube via the radial direction, thus providing part of the heat load necessary to drive the endothermic catalytic reactions in the inner membrane tube.

Permeation of reaction products through the membrane tubes, especially hydrogen through the inner membrane tube, shifts the thermodynamic equilibrium conversion of reactant species to the product side and produces excess hydrogen and carbon oxide products within the catalytic reaction zone (4). Outer membrane tube thereby, serves as a final permeable medium for the recovery of highly pure hydrogen product for use in hydrogen utilization applications. Outer metal membrane tube serves also as a separation medium for hydrogen out of the central annular zone between the two membrane tubes, so that partial pressure of hydrogen lowers substantially along the annular zone, and therefore continuous driving force exists for hydrogen permeation from the catalytic reaction zone (4) to the central annular zone (8). As an alternative to the invented design, for low operating gas reforming and dehydrogenation temperatures (e.g., between 200-400°C) in the absence of steam as a reactant, the inner membrane tube (2)

can be made by porous inorganic or inorganic-metal materials and the outer membrane tube (1) can be made by organic materials which withstand high temperature (i.e., materials with high glass transition temperature, Tg), and are permselective to both hydrogen and carbon dioxide which permeate through the inner tube (2) and flow along the central annular zone (8). The mixture of $H_2$ and $CO_2$ can be used directly in chemical synthesis applications such as this of alternative methanol synthesis via the reaction: $CO_2+3H_2=CH_3OH+H_2O$, and as direct feed in molten carbonate fuel cells via the overall electrochemical reaction: $H_2+CO_2+1/2O_2 \rightarrow H_2O+CO_2$. Moreover mixtures of $H_2$ and $CO_2$ can be converted to $CH_4$ or CO, if a special application requires, via the methanation or reverse water gas shift reactions respectively given below:

$$CO_2+4H_2=CH_4+2H_2O, \quad CO_2+H_2=CO+H_2O$$

The external (outer) membrane (1) serves also as a backup membrane medium in case the inner membrane develops cracks or defects and its permeability to various gases increases. In this case, the outer membrane will selectively separate specific gases based on the selected membrane material as described above. Moreover, operational and maintenance service for replacing old or damaged membrane and outer non-membrane tubes becomes easier with the proposed design, because each part of the reactor is interconnected with the rest and can be disassembled and assembled accordingly.

Heating of the reformer or reactor is achieved via tubes (6) arranged symmetrically around the reactor axis and operated in the gas combustion regime by flowing waste type hydrocarbons or hydrocarbon-hydrogen mixtures mixed with oxygen or air. Unreacted hydrocarbons, carbon monoxide, non-permeate hydrogen or any mixture of these species from the reformer outlet can be recycled as well into the heating combustion tubes (6). In an alternative heating configuration, a single cylindrical tube having the shape of a tube or a coil is located along the reactor axis and can be operated by using same quality of combusted gases. In a third alternative configuration the symmetrically located tubes with flowing gas can be replaced by cylindrical electric heaters, heating bars or coils.

Fig.2, shows multiple double permeable wall reactors of those described in Fig.1, but without the far outer impermeable tube (7), which are placed symmetrically inside a larger impermeable tube (A1), to create a multiple tube reformer with a common external area for collecting final permeate hydrogen.

Fig.3 shows another developed reformer or reactor design to be used in steam and carbon dioxide reforming of hydrocarbons, steam reforming of alcohols, water gas shift and dehydrogenation reactions. Reformer or reactor consists of a most outer impermeable tubular cylinder (shell) (1) which is hollow inside in order to nest two more concentric tubular cylinders, a next inner one (2) and finally a most-inner (3) which both are made by permeable materials. Most outer cylinder (1) is made by impermeable stainless steel or alloys, but next-inner cylinder (2) consists of metal, metal alloys, non-porous and porous inorganics, porous inorganic-metals or carbon materials such as those described in embodiment of Fig.1.

The derived concentric cylindrical assembly has proper inlet and outlet fittings for feeding the feedstocks and discharging the post-reaction species. Proper inlet and outlet

fittings are interconnected with the different sites of the cylindrical assembly. Fittings are connected to the annular space between most-outer and next-inner cylinders to deliver and collect gases flowing in this space. Additional independent fittings are connected to the annular space between the next-inner and most-inner cylinders to deliver and collect gases flowing in this space. Additional independent fittings are connected to the tubular space of the most-inner cylinder to deliver and collect gases flowing in this space. The fittings are made in such a manner so that they can seal in a leak-free manner each corresponding space, and the overall cross section of the double permeable wall cylindrical tube assembly. Before the fittings are applied and tighten, the annular space between the most outer (external) and next-inner cylinders is filled with the proper reaction catalyst in pellet or particle form to make the catalytic reaction zone (4) . Proper catalyst is used for each reforming, water gas shift and dehydrogenation reactions. Catalysts used in these reactions are same with these mentioned above in description of embodiment of Fig.1.

In steam, $CO_2$ reforming of hydrocarbons, steam reforming of alcohols, water gas shift and paraffin dehydrogenation reactions, hydrogen is removed along the next-inner lateral cylindrical metal membrane surface (2), with carbon monoxide, carbon dioxide, steam, hydrocarbons, alcohols to possibly also permeate through inner lateral membrane surface in a lesser degree than hydrogen depending on the membrane material used. An inert carrier gas such as argon, nitrogen, steam or a mixture of those gases, may flows along the permeate annulus, between tubes (2) and (3), through suitable inlet fittings, to carry the permeate components at a specific pressure value. Permeate hydrogen is further removed through permeation along the lateral surface of most-inner membrane tube (3) so that the final permeated stream contains pure hydrogen only, with pure hydrogen to be used in various applications including feed to synthesis reactors, gas turbines and engines, and fuel cells.

The most-inner membrane tube (3) is made by a metal, metal alloy, non-porous inorganic or carbon membrane which allows only hydrogen to permeate through and therefore purifies hydrogen from the permeating carbon oxides, steam and hydrocarbons, flowing in the annular zone created between the next-inner and most-inner cylindrical tubes. Membrane tubes (2) and (3) can be made with similar manufacturing techniques as those described in embodiment of Fig.1. The most-inner membrane tube can be either empty or may contain a selective catalyst (5) which converts permeate hydrogen combined with another component flowing through the inner bore of this tube. Such a flowing (sweep) component can be an unsaturated hydrocarbon (e.g., alkenes, alkynes) for conversion to saturated hydrocarbons, after reaction with the permeate hydrogen in an exothermic reaction. Flowing (sweep) component for hydrogenation by the permeate hydrogen can be also carbon monoxide for direct production of methanol or gasoline hydrocarbons (through Fischer-Tropsch synthesis) in exothermic type reactions. Flowing (sweep) gas can be nitrogen for exothermic ammonia synthesis after combination with the permeate hydrogen. Other combination reactions with permeate hydrogen can be these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides and these for reduction of nitroalkanes and aromatic nitro compounds to corresponding primary amines. Alternatively, pure permeate hydrogen can be used as direct feed in

hydrogen based turbines and engines, fuel cells, and other power generation equipment. The heat generated by exothermic reactions in the most-inner cylindrical bore, may be transferred into the catalytic reaction zone of the outer membrane cylinder via the radial direction, thus providing part of the heat load necessary to drive the endothermic catalytic reactions in catalyst bed (4) located within the outer membrane cylinder.

Permeation of hydrogen through the first inner membrane tube, shifts the thermodynamic equilibrium conversion of reactant species to the product side and produces excess hydrogen and carbon oxide products for reforming and water gas shift reactions, and hydrogen only for paraffin dehydrogenation reactions.

Most-inner membrane tube thereby, serves as a final permeable medium for the recovery of highly pure hydrogen product for use in hydrogen utilization applications. Most-inner metal membrane tube serves also as a separation medium for hydrogen out of the annular zone between the two hollow cylindrical membrane tubes, so that partial pressure of hydrogen lowers substantially along the annular zone, and therefore continuous driving force exists for hydrogen permeation from the enclosed catalytic reaction zone (4) to the central annular zone (7), through the next inner membrane tube (2).

As an alternative to the invented design, for low operating gas reforming and dehydrogenation reaction temperatures (e.g., between 200-400°C) and in the absence of steam as a reactant, the next-inner membrane tube (2) can be made by porous inorganic or inorganic-metal materials which are permeable to several species diffusing out of the reaction zone (4), and the most-inner membrane tube (3) can be made by organic materials which withstand high temperatures (have high glass transition temperature, Tg) and are permselective to both hydrogen and carbon dioxide species which flow along the central annular zone (7). The binary permeate mixture of $H_2$ and $CO_2$ can be used in applications described already in embodiment of Fig.1.

The most-inner membrane serves also as a backup membrane medium in case the first-inner membrane develops cracks or defects and its permeability to various gases increases. In this case, the most-inner membrane will selectively separate specific gases based on the selected membrane material as described above. Moreover, operational and maintenance service for replacing old or damaged membrane and outer non-membrane tubes becomes easier with the proposed design, because each part of the reactor is interconnected with the rest and can be disassembled and assembled accordingly.

Heating of the described reformer or reactor is achieved via external heat provision (6). The external to the reformer combustion regime can be fueled by flowing waste type hydrocarbons or hydrocarbon-hydrogen mixtures mixed with oxygen or air. Unreacted hydrocarbons, carbon monoxide product, non-permeate hydrogen product, or any mixture of these post-reaction species coming out of the cylindrical reformer outlet connected with the catalyst zone (4), can be recycled as well into the external combustion-heating zone (6). Optionally, external heating of most-outer shell (1) can be provided by cylindrical type heaters or heating elements (i.e., made by ceramic, composite materials) in contact with the shell.

Fig.4, shows multiple double permeable wall cylinder reactors of those described in Fig.3, which are placed symmetrically inside a larger impermeable tube (shell) (A1), to create a multiple tube reformer with a common external heating area.

Fig.5 shows a cross section of a reformer or dehydrogenation reactor which consists of multiple cylindrical hollow polymer membrane tubes or fibers (1) nested within an outer impermeable metal cylindrical tube (2) which also contains the catalyst (3) in particle or pellet form, for the specific reactions mentioned below.

Reacting gas feedstocks free of steam such as $CO_2$ and hydrocarbons also paraffin hydrocarbons are fed within the catalyst zone (3) through special inlet fittings and they react in the catalyst to produce hydrogen and carbon monoxide or hydrogen and olefins. Optionally, small volumetric quantities of hydrogen can be added into above feedstocks in inlet of the reactor assembly, to prevent heavy catalyst deactivation in the reactor inlet, wherein propensity for hydrocarbon cracking into carbon is high in absence of any hydrogen. The $CO_2$ (dry) reforming or dehydrogenation catalysts are the same metallic type with those described in embodiment of Fig.1. Steam is avoided as a reactant in the reactor to avoid long term plasticization and structural damage of membrane tubes and loss of related permeability and selectivity properties.

Hydrogen product from these reactions is removed along the surface of the multiple membrane tubes (1), wherein the membranes are made by organic polymer or composite polymer membranes. Traces of carbon monoxide, carbon dioxide, product steam, olefins, and unreacted hydrocarbons may also permeate through the membrane tubes (1) in a lesser degree than hydrogen. The permeate gas mixture is continuously removed through the inner side of the membrane tubes and flows into a common impermeable metal shell which is interconnected with all the membrane tubes and sealed from the gases flowing into the catalytic reaction side (3). Optionally, a flowing component can flow along the inner membrane tube to sweep and dilute the permeate gas as it flows through the tubes.

In an optional design, catalyst in form of pellets or particles (4) can be contained within the inner side of the polymer membrane tubes to carry suitable catalytic reactions (such as hydrogenations) in which one of the reacting species is permeate hydrogen and the other reaction species are contained within the flowing gas. Such a flowing (sweep) component can be an unsaturated hydrocarbon (e.g., alkenes, alkynes) for conversion to saturated hydrocarbons, after reaction with hydrogen, in an exothermic reaction. Flowing (sweep) component can also be carbon monoxide for direct production of methanol or gasoline (through Fischer-Tropsch synthesis) after combination with the permeate hydrogen, in exothermic type reactions. Flowing gas can be nitrogen for exothermic ammonia synthesis after its combination with the permeate hydrogen. Other combination reactions with permeate hydrogen over specific metallic catalysts, can be these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides and these for reduction of nitroalkanes and aromatic nitro compounds to corresponding primary amines. Part of the heat generated by the exothermic reactions in the inner side of the tubes, may be transferred across the membranes, into the common catalytic reaction zone

(3) surrounding the multiple membrane tubes, thus providing part of the heat load necessary to drive the endothermic catalytic reactions in catalyst zone (3).

Permeation of reaction products and especially hydrogen through the membrane tubes (1), shifts the thermodynamic equilibrium conversion of reactant species to the product side and produces excess hydrogen, carbon oxide, and olefins respectively within the catalytic reaction zone (3). Permeate collected hydrogen through the inner tubes (1), can be used in chemical synthesis or fuel applications as described in embodiment of Fig.1.

As an alternative to the disclosed design, for low operating reforming and dehydrogenation temperatures (e.g., between 200-400°C), the inner tubes (1) can be made by materials which are permselective to both hydrogen and carbon dioxide products which permeate along the surface of the tubes (1). The separated mixture of $H_2$ and $CO_2$ can be used in applications described in embodiment of Fig.1.

The main heating of the catalyst zone (3), is achieved via external heating (5) of the impermeable most-outer reactor shell (2) through combustion of flowing waste type hydrocarbons or hydrocarbon-hydrogen mixtures mixed with oxygen or air. Unreacted hydrocarbons, carbon monoxide, non-permeate hydrogen or any mixture of these species coming out of the outlet of catalytic zone (3) can be recycled as well into the external combustion zone (5). Optionally, external heating of outer shell (2) can be provided by any type of cylindrical type heaters or heating elements (i.e., ceramic, composite).

Fig.6, depicts a system of catalytic permreactor with consecutive permeator (or optionally a permreactor) and optionally another final consecutive reactor, for conducting reforming and gas shift reactions. In Fig.6, stream 1 contains hydrocarbon feedstocks such as methane ($CH_4$), higher alkanes (paraffins), naphtha, and natural gas, mixed with steam and $CO_2$ and introduced in catalytic permreactor A for conducting simultaneously reactions (1), (2) and (3), or mixed with $CO_2$ only for conducting reactions (2) and (3). Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation from hydrocarbon cracking especially in the inlet of permreactor A.

Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with $H_2$ to be separated in permeate stream 1b via valve A1, in the general case. $H_2$ and $CO_2$ combined, can be separated in permeate stream in special applications, if an organic membrane is used in permreactor A. The rejected exit stream from the permreactor may contain product CO together with unreacted steam ($H_2O(g)$), $CO_2$, and hydrocarbon, and non-permeate $H_2$. This stream becomes stream 2 and enters into heat exchanger B, where the unreacted steam is removed through condensation, and by the heat exchanging process new steam is generated in stream 6 from the water or steam of stream 5. Stream 6, can provide steam in permreactor A and reactor E through streams 9 and 10,18 respectively, in an alternative or simultaneous manner via use of valves B1,E1. The steam in 6 aquires the exchanged heat load from stream 2, the hot gas effluent of permeable reformer A, and thus its derived streams 9,10,18 can be mixed directly with streams 1 and 12 which are fed directly into reactors A and E respectively.

Steam from 6 is used via streams 10,18 and valves B1,E1 to provide the initial steam content in reformer E. Stream 7, passes through a bed of particles C (moisture adsorbent) to remove any non-condensed traces of moisture and through exit stream 8 enters into membrane permeator D. Stream 8, contains CO product, non-permeate $H_2$ product, unreacted hydrocarbon (e.g., $CH_4$) and $CO_2$ gases and has been cooled at the operating temperature of permeator D. $H_2$ or both $H_2$ and $CO_2$ are removed in permeate stream 11 of permeator D, through the permselective action of a metal, non-porous inorganic, carbon, or organic membrane respectively. Non permeating stream containing hydrocarbon (e.g., $CH_4$), CO and $CO_2$ or hydrocarbon and CO respectively, depending on the type of membrane used in permeator D, exits from permeator D, through stream 12 as reject stream. Stream 12 enters into reformer E, for conducting simultaneously reforming and water shift reactions selected from the group of reactions (1), (2) and (3), and be converted to final $H_2$, CO, $CO_2$ or $H_2$ and $CO_2$ only products, depending on the feed composition of stream 12 in reformer E. Steam in reformer E is provided via stream 18. Unreacted steam is removed from exit stream 15 by passing this stream through heat exchanger F. Steam is generated from water or steam of stream 16 and via streams 17,18 and valve E1, the generated steam is fed into inlet of reformer E. Exit stream 19 contains $H_2$, CO, $CO_2$ or $H_2$, $CO_2$ products and traces of unreacted hydrocarbons, depending on the operating conditions, that is the temperature, pressure, space velocity and feed composition of streams 12 and 18, of reformer E. Reformer E, can be replaced by a permeable reformer E similar to permeable reformer A, wherein $H_2$ is separated in permeate and the reject exit stream 19 consists of CO and $CO_2$ or $CO_2$ only.

Reformers A and E are endothermic and flue gas streams 3,4 and 13,14 respectively are used to provide the necessary heat content to drive parallel reactions (1), (2) and (3) to completion. The two reformers can operate at same or different temperature and pressure conditions.

If conversion is high in permeable reformer A under certain operating conditions, the product in stream 2 is mainly CO and $H_2$ which can be used directly as synthesis gas in methanol synthesis via the direct exothermic reaction: $CO+2H_2=CH_3OH$, also in Fischer-Tropsch type reactions for production of gasoline type hydrocarbons, and as fuel in gas turbines and engines and solid oxide fuel cells for power generation.

If the overall process consists of two reformers and the intermediate permeator, and the final product is a $H_2$ and $CO_2$ mixture in exit stream 19, it can be used separately or it can be mixed with stream 11 to make a combined $H_2$ and $CO_2$ stream. This combined $H_2$, $CO_2$ mixture can be used for direct methanol synthesis via the exothermic reaction: $3H_2+CO_2=CH_3OH(g)+H_2O(g)$. Also, the $H_2$, $CO_2$ mixture can be used as direct feed in molten carbonate fuel cells for electricity generation via the overall electrochemical reaction:

$$H_2+CO_2+1/2O_2 \text{ (cathode)} \longrightarrow H_2O+CO_2 \text{ (anode)}$$

Alternatively, $CO_2$ can be condensed cryogenically from the binary mixture and pure hydrogen can be produced. Final $H_2$ product can be used for chemical synthesis or as direct feed in fuel cells and gas turbines and engines for power generation applications (e.g., transportation, stationary). Applicable hydrogen driven fuel cells for utilizing the pure separated hydogen from the process, include proton exchange membrane (PEM),

solid oxide (SOFC), molten carbonate (MCFC), alkaline (AFC), phosphoric acid (PAFC) and modifications and combinations of these fuel cells.

Generated hydrogen product from the process can be combined with an unsaturated hydrocarbon (e.g., alkenes, alkynes) for conversion to saturated hydrocarbons in an exothermic type reaction. Also, with carbon monoxide for direct production of methanol (as described above) or gasoline (through Fischer-Tropsch synthesis) in exothermic type reactions. Hydrogen can be also combined with nitrogen for exothermic ammonia synthesis. Other combination (synthesis) reactions with permeate hydrogen can be these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides and these for reduction of nitroalkanes and aromatic nitro compounds to corresponding primary amines.

The described process is able to overcome the thermodynamic equilibrium limitations of hydrocarbon ($CH_4$) and $CO_2$ reactant conversion, through the removal of $H_2$ only, or of $H_2$ and $CO_2$ gases in membrane permreactor A and permeator D. The calorific value of the obtained $H_2$, CO product in permreactor A, is higher than this of the reactant hydrocarbon (e.g., $CH_4$), $CO_2$ and steam and the endothermic heat of reaction is stored in the products which can be subsequently used as fuels or in chemical synthesis.

Assuming 100% conversion of reactions (1) and (3) and reaction (2) in equilibrium in permreactor A, 2 mol of $CH_4$ (with heat of combustion: 425.6 kcal), 1 mol of $CO_2$ (with no heat of combustion), and 1 mol of $H_2O(g)$ (with no heat of combustion), produce 3 mol of CO (with heat of combustion: 202.8 kcal) and 5 mol of $H_2$ (with heat of combustion: 341.5 kcal). These values are at 25°C. This corresponds to about 28% increase in calorific value for the product. Endothermic heat can be provided in reformers A and E through the combustion of flue or waste gases or unreacted recycled hydrocarbons coming out of the exit of reaction zone of reformers A and E as also described in Figs.1 and 3 above.

In an alternative design, permeator D is replaced by a catalytic permreactor D wherein the water gas shift reaction occurs if stream 8 is rich in product CO. In such case permreactor D is made by metal, non-porous inorganic, or carbon membranes to separate only hydrogen in permeate. Exit reject stream 12 from permreactor D contains product $CO_2$ and unreacted steam and can be recycled in the first reforming permreactor or used in downstream applications either as a mixture or as pure $CO_2$ after condensation of the steam.

Fig.7, describes a similar embodiment with the one described in Fig.6, but feed stream 1 contains carbon monoxide (CO) only, mixed with steam, and introduced in catalytic permreactor A which is filled with catalyst particles to conduct the water gas shift reaction only.

Catalytic permeable water gas shift reactor A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with $H_2$ to be separated in permeate stream 1b via valve A1, in the general case. $H_2$ and $CO_2$ combined, can be separated in permeate stream for special applications, if an organic membrane is used in permreactor A. The rejected exit stream from the permreactor contains product CO together with unreacted steam ($H_2O(g)$) and non-permeate $H_2$. This stream becomes stream 2 and enters into heat

exchanger B, where the unreacted steam is removed through condensation, and by the heat exchanging process new steam is generated in stream 6 from the water or steam of stream 5. Stream 6, can provide steam in permreactor A and reactor E through streams 4 and 11,13 respectively, in an alternative or simultaneous manner via use of valves B1,F1. The steam in 6 aquires the exchanged heat load from stream 2, the hot gas effluent of permeable reactor A, and thus its derived streams 4,11,13 can be mixed directly with streams 1 and 12 which are fed directly into reactors A and E respectively.

Steam from 6 is used via streams 11,13 and valve F1 to provide initial steam in reactor E. Stream 7 passes through a bed of particles (moisture adsorbent) C to remove any non-condensed traces of moisture and through exit stream 8 enters into membrane permeator D. Stream 8 contains non-permeate product $H_2$, product $CO_2$ and unreacted CO gases and has been cooled at the temperature of permeator D. $H_2$ and $CO_2$ are removed in permeate stream 9 through permselective action of membrane in permeator D. Non permeating CO exits from permeator through stream 10 which can be called a reject stream. Stream 10 can be recycled via valve D1 and stream 3 into the first permeable shift reactor A for contiuous shift reaction and conversion to $H_2$ and $CO_2$ products. Alternatively, by use of same valve D1, stream 10 becomes 12 which enters into reactor E for additional shift reaction (2), and conversion to final $H_2$, $CO_2$ products. Steam in E is provided via stream 13. Unreacted steam is removed from exit stream 14 by passing this stream through heat exchanger F. New steam is generated from water or steam of stream 15 and via streams 16,13 and valve F1 is fed into inlet of reactor E. Exit stream 17 contains $H_2$, $CO_2$ products and traces of unreacted CO depending on the operating conditions, that is the temperature, pressure and feed composition of streams 12 and 13, of reactor E.

Shift reactors A and E are exothermic and no heat input is necessary as with the previous endothermic reformers described in previous embodiments. Stream 1 needs to be preheated in temperature of permeable reactor A before entering into reactor. Using the heat content of streams 2 and 14 exiting from the reactors to provide the necessary heat content in the feed streams 4 and 13 entering into the reactors, the entire process operates in an autothermic way with no additional heat input necessary. The two shift reactors can operate at same or different temperature and pressure conditions.

Exit stream 17 can be used separately or it can be mixed with stream 9 to make a combined $H_2$ and $CO_2$ stream to be used for chemical synthesis or as fuel in applications similar to the ones mentioned above for the reforming reactors. Pure $H_2$ from the process can be recovered after the $CO_2$ condensation and removal. Pure hydrogen from the process, can be used as fuel or in chemical synthesis applications, as described in embodiment of Fig.6 above.

The described shift process is able to overcome the equilibrium CO reactant conversion limitations, through removal of $H_2$ in permreactor A and intermediate removal of $H_2$ and $CO_2$ products in permeator D. Thus, the process increases CO conversion and $H_2$, $CO_2$ yields above those obtained in conventional water gas shift reaction separation systems for production of $H_2$ and $CO_2$. By use of the two heat

Fig.8 is an embodiment of a system of catalytic permreactor with consecutive permeator for conducting paraffin (alkane) dehydrogenation reactions. In Fig.8, stream 1 contains hydrocarbon feedstocks such as ethane, propane, n-butane, i-butane, naphtha, or liquid alkanes such as pentane, hexane, heptane. Liquid alkanes are vaporized by preheating before fed into catalytic permeable dehydrogenator A. Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation in the catalyst from hydrocarbon cracking especially in the inlet of permreactor A.

Catalytic permeable dehydrogenator A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with $H_2$ to be separated in permeate stream 1b via valve A1. The rejected exit stream from permreactor A contains unreacted paraffins, product olefins, and non-permeate hydrogen. This stream becomes stream 2 and optionally passes through heat exchanger B, where by the heat exchanging process steam is generated in stream 6 from the water or steam of stream 5 to be used in steam requiring applications.

Stream 7, enters into membrane permeator C. $H_2$ is removed in permeate stream 8 of permeator C, through the permselective action of a metal, non-porous inorganic, carbon or organic membrane. Non permeating stream containing hydrocarbons (product olefins and traces of unreacted paraffins) exits from permeator C, through stream 9 as reject stream. Stream 9 has composition dependent on the paraffin conversion in permreactor A and the hydrogen separation efficiency in permeator C. By optimizing these two parameters, pure olefins can be produced in stream 9, to be used as direct feed in polyolefin reactors E for polyolefin production (i.e., polyethylene, polypropylene) exiting from stream 10. Olefins from stream 9 are also used as direct feed in synthesis reactors, such as ethylene for ethylene oxide and ethylene glycol production, propylene for propylene oxide and propylene glycol production, isobutylene for oxygenated gasoline production. Produced pure hydrogen from the described process can be used into same fuel and synthesis applications as described in embodiment of Figs.1 and 3.

Paraffin dehydrogenation reactions are endothermic, and reactor A receives heat from flue gas streams 3,4 to drive dehydrogenation reactions (4) to completion.

The described process is able to overcome the thermodynamic equilibrium limitations of paraffin hydrocarbon conversion met in conventional reactors, through the removal of product $H_2$ in membrane permreactor A and permeator C. Endothermic heat can be provided in dehydrogenator A through the combustion of flue or waste hydrocarbons or unreacted recycled hydrocarbons from the reaction zone of reactor A as also described in embodiments of Figs.1,3 and 5 above.

Permeable dehydrogenator A can be substituted by non-permeable (e.g., non-porous stainless steel wall) dehydrogenator A. Valve A1 and stream 1b are eliminated and all post-reaction gases exit from stream 2. Permeator C still operates in same function as described above.

Fig.9, is an embodiment which is related with these described in Figs.6 and 7, but with stream 1 to contain hydrocarbon feedstocks such as methane or higher alkanes such as naphtha and natural gas, also alcohol feedstocks such as methanol, ethanol, propanol,

butanol mixed with steam only and introduced in catalytic permreactor A which is filled with catalyst particles to conduct the methane steam reforming reaction (1) and the simultaneously occurring water gas shift reaction (2). Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation from hydrocarbon cracking especially in the inlet of the reactor A.

Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with $H_2$ to be separated in permeate stream 1b via valve A1, in the general case. $H_2$ and $CO_2$ combined, can be separated in permeate stream in special applications, if an organic membrane is used in permreactor A. The rejected exit stream from the permreactor may contain product $CO_2$, CO, unreacted steam ($H_2O(g)$) and hydrocarbon, and non-permeate $H_2$. This stream becomes stream 2 and enters into heat exchanger B, where the unreacted steam is removed through condensation, and by the heat exchanging process new steam is generated in stream 8 from the water or steam of stream 7. Stream 8, can provide steam in permreactor A and reactor E through streams 6 and 10,20 respectively, in an alternative or simultaneous manner via use of valves B1,E1. The steam in 8 aquires the exchanged heat load from stream 2, the hot gas effluent from permeable reformer A, and thus its derived streams 6,10,20 can be mixed directly with streams 1 and 14 which are fed directly into reactors A and E respectively.

Steam from 8 is used via streams 10,20 and valve E1 to provide initial steam in reformer E. Stream 9 passes through a bed of particles (moisture adsorbent) C to remove any non-condensed traces of moisture and through exit stream 11 enters into membrane permeator D. Stream 11 has been cooled in temperature of permeator D and contains CO, $CO_2$, unreacted hydrocarbon, non-permeate $H_2$ gas species.

$H_2$ or both $H_2$ and $CO_2$ are removed in permeate stream 12 of permeator D, through the permselective action of a metal, non-porous inorganic, carbon or organic membrane respectively. Non permeating stream containing hydrocarbon (e.g., $CH_4$), CO and $CO_2$ or hydrocarbon and CO respectively, depending on the type of membrane used in permeator D, exits from permeator D, through stream 13 as reject stream. In case wherein stream 13 contains hydrocarbon and CO it can be recycled via valve D1 and stream 5 into first permeable reformer A for continuous reforming and conversion to main $H_2$ and $CO_2$ products. Alternatively, by use of valve D1, stream 13 becomes stream 14 which enters into steam reformer E for additional reforming and shift reactions, via reactions (1) and (2) and additional conversion to $H_2$ and $CO_2$ products. In case wherein stream 13 contains hydrocarbon, CO and $CO_2$, using valve D1, stream 13 becomes stream 14 which enters into modified steam and $CO_2$ reformer E for additional reforming and shift reactions, via reactions (1), (2) and (3) and conversion to H2, CO, $CO_2$ products. Reformer E, can be replaced by a permeable reformer E similar to permeable reformer A, wherein $H_2$ is separated in permeate and the reject exit stream 17 consists of product CO and $CO_2$ or $CO_2$ only.

Reformers A and E are endothermic and flue gas streams 3,4 and 15,16 respectively are used to provide the necessary heat content to drive parallel reactions (1), (2) and (3) to completion. The two reformers can operate at same or different reaction temperature and pressure conditions.

If conversion is high in permeable steam reformer A under certain operating conditions, the product in stream 2 is mainly $CO_2$ and non-permeate $H_2$ which can be used directly in applications described already in embodiment of Figs. 1 and 3.

If the overall process consists of two reformers and the intermediate permeator, and the final product is $H_2$ and $CO_2$ in exit stream 21, this product can be used separately or it can be mixed with stream 12 to make a combined $H_2$ and $CO_2$ stream to be used in similar applications.

Alternatively, $CO_2$ can be condensed cryogenically from the binary mixture and pure hydrogen product is produced. Final $H_2$ product can be used for chemical synthesis or as direct feed in fuel cells and gas turbines and engines for power generation applications (e.g., transportation, stationary), same to these described in embodiment of Fig.6.

The described process is able to overcome the thermodynamic equilibrium limitations of hydrocarbon ($CH_4$) and steam reactant conversion, through the removal of $H_2$ product only, or of the combined $H_2$ and $CO_2$ products in membrane permreactor A and permeator D. The calorific value of the obtained $H_2$, $CO_2$ product in permreactor A, is higher than this of the reactant hydrocarbon (e.g., $CH_4$) and steam mixture, because the provided endothermic heat of reaction is stored in the products and can be subsequently released by using products as fuels or in chemical synthesis.

Assuming 100% conversion of reactions (1) and (2), 1 mol of $CH_4$ (with heat of combustion: 212.8 kcal) and 2 mol of $H_2O(g)$ (with no heat of combustion) generate 1 mol of $CO_2$ (with no heat of combustion) and 4 mol of $H_2$ (with heat of combustion: 273.3 kcal). These values are at 25°C. This corresponds to about 28% increase in calorific value for the product gases. By providing external heat through flue or waste gas input in the reformers and with the described two heat exchangers in place, the energy requirement of the one reactor-one permeator or two reactor-one permeator cascades is fulfilled and the processes operates in a thermally independent manner providing for an energy efficient design. Endothermic heat can be provided in reformers A and E through the combustion of flue or waste gases or unreacted recycled hydrocarbons from the reaction zone of reformers A and E, as also described in Figs.1,3,5 above.

Fig.10, is an embodiment of a steam and $CO_2$ hydrocarbon reforming process which includes a permeable reformer or a non-permeable reformer followed by a cryogenic separator for separation of certain post-reaction gases exiting from the reject exit of the reformer. In Fig.10, stream 1 is introduced into catalytic permreactor A, containing hydrocarbon feedstocks such as methane ($CH_4$) mixed with steam and $CO_2$ for conducting simultaneously reactions (1), (2) and (3), or mixed with $CO_2$ only for conducting reactions (2) and (3). Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation from methane cracking especially in the inlet of permreactor A.

Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with $H_2$ to be separated from the reformer, and exit in permeate stream 1b via valve A1. The rejected exit stream from the permreactor contains product CO together with unreacted steam ($H_2O(g)$), $CO_2$, and hydrocarbon, and non-permeate $H_2$. This stream becomes stream 2 and enters into a steam condenser C wherein

the unreacted steam is condensed and by the heat exchanging process new steam is generated in steam 17 from the water or steam of stream 16. Steam through stream 17 is recycled into stream 1 in inlet of reformer A. Stream 5 free of steam, exits from condenser C and enters into cryogenic separator B, which operates at a temperature lower than the boiling temperature of carbon dioxide and hydrocarbons so that these compounds are separated as liquids and collected in the bottom of the separator (operating cryogenic temperature of the separator is a negative number which has larger absolute value than the absolute value of any of the boiling points of the liquified components above). However, operating cryogenic temperature of separator is higher than the boiling points of carbon monoxide and hydrogen so that these compounds remain in the gas phase and exit from the separator as a gas mixture (operating cryogenic temperature of the separator is a negative number which has smaller absolute value than the absolute value of the boiling points of both hydrogen and carbon monoxide). Liquified components exit via stream 7 through valve B1. Gas phase hydrogen and carbon monoxide exit as stream 6 via valve B2. Liquified stream 7 can be recycled into the feed stream of reformer A (stream 1) via stream 8 after evaporation in evaporator D. Alternatively, stream 8 can be further processed in another reforming reactor by becoming stream 9 which enters into reformer E, for additional steam and $CO_2$ reforming of any remaining hydrocarbons via reactions (1), (2) and (3). Optional, steam in reformer E is provided via stream 18. Stream 10 exiting the reformer can optionally condense the containing unreacted steam by passing through the heat exchanger F. Inlet stream 11 contains water which becomes steam in stream 12 after passing through F. Steam in stream 12 can optionally fed into reformer E via valve E1. Stream 13 exiting the heat exchanger F is dry, and contains $H_2$ and CO as main products with traces of unreacted hydrocarbons and $CO_2$ depending on the operating temperature and pressure of the reformer E and the composition of feed streams 10 and 12.

Recovered $H_2$ and CO in stream 13 can be either used separately or optionally be combined with stream 6 from the separator to make one stream to be used as fuel or in chemical synthesis. Direct application of the produced $H_2$ and CO mixture is in methanol synthesis via the direct exothermic reaction: $CO+2H_2=CH_3OH$, also in Fischer-Tropsch type reactions for production of gasoline type hydrocarbons, and as fuel in gas turbines and engines and solid oxide fuel cells for power generation. Similarly, $H_2$ recovered in stream 5, can be used as fuel or in chemical synthesis, as described in embodiment of Fig.6. The described process is able to overcome the thermodynamic equilibrium limitations of hydrocarbon (e.g., $CH_4$), steam and $CO_2$ reactant conversion, through the removal of $H_2$ and $H_2$ and CO gases in membrane permreactor A and cryogenic separator B respectively. Endothermic heat in reformers A and E is provided through gas streams 3,4 and 14,15 respectively. Streams 3, 14 can be fed by a bypass stream of exit stream 2, as also described in embodiments of Figs.1,3,5. The reformer A can be optionally substituted by a non-permeable reformer A, wherein stream 1b and valve A1 are eliminated and all product $H_2$ is included in post-reaction mixture entering through stream 2 into cryogenic separator B.

Fig.11, is a modified embodiment of the process described in Fig.6. It applies to complete conversion of hydrocarbon (i.e., $CH_4$) and $CO_2$ reactants of stream 1, within the

permeable reformer A, to $H_2$ and CO products. The occurring reactions are (1),(2),(3) or (2),(3) only. Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with $H_2$ to be separated in permeate stream 3 via valve A1. Exiting from the permreactor, stream 2, containing only CO and non-permeating $H_2$, or CO, non-permeating $H_2$, and traces of unreacted steam, enters into a solid oxide fuel cell (SOFC) unit B. Stream 2 is directed in the anode of the solid oxide cell, and consists the fuel constituent of the fuel cell. $O_2$ in stream 4, is directed in the cathode of the fuel cell and consist the oxidant, for the well known electrochemical reaction conducted within the cell with electric current generation:

In Anode: $H2 + O^{2-} \longrightarrow H2O + 2e^-$

In Cathode: $O2 + 4e^- \longrightarrow 2O^{2-}$

Optionally, part of hydrogen from permeate stream 3, can be fed into stream 2, via bypass stream 3b, to adjust the composition of $H_2$ in stream 2 to that required to feed the fuel cell B. The reformer A can be optionally substituted by a non-permeable reformer A, wherein all product H2 is included in exit stream 2. Flue gas streams 5 and 6, are used to provide the endothermic heat content into the reformer A. Stream 5 can be fed by a bypass stream of exit stream 2, as also described in embodiments of Figs.1,3,5. Permeable reformer A can be substituted by a non-permeable (e.g., stainless steel) reformer A. Valve A1 and stream 3, 3b are eliminated and all post-reaction gases exit from stream 2. Fuel cell B still operates in same function as described above.

Fig.12, is an embodiment which describes a modified operation of the process described in Fig.6. It applies to complete conversion of hydrocarbon (i.e., $CH_4$) and $CO_2$ reactants of stream 1, within the permeable reformer A, to $H_2$ and CO products. The occurring reactions within the reformer are (1),(2),(3) or (2),(3) only. Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with $H_2$ to be separated in permeate stream 1b via valve A1. Exiting from the permreactor, stream 2, containing only CO and non-permeating $H_2$, or CO, non-permeating $H_2$, and traces of unreacted steam, passes through heat exchanger B and moisture adsorbent C to remove unreacted steam, and enters into permeator D as a dry stream. Hydrogen is separated in stream 11 from carbon monoxide, rejected by the membrane, and exiting via stream 12. Carbon monoxide, via stream 12, can be optionally fed into a consecutive water gas shift reactor E for conversion to final $H_2$ and $CO_2$ products. A heat exchanger F is used in exit of the water gas shift reactor E, to remove any unreacted steam, with final stream 15 to contain only $H_2$ and $CO_2$. The reformer A can be optionally substituted by a non-permeable reformer A, wherein all reaction product $H_2$ is included in exit stream 2 and stream 1b, valve A1 are eliminated.

Hydrogen from stream 11 can be used in applications mentioned already in embodiment described in Fig.6 and Fig.9. Similarly CO from stream 12, or $H_2$ and $CO_2$ from stream 15 can be used in aforementioned applications described already in embodiments of Figs.6,9 and 10.

Fig.13, is an embodiment of a modified process of the process described in Fig.6. It pertains to methanol production from the products of the reforming reaction occurring in reactor A, and the subsequent utilization of methanol in a methanol-steam reforming

reactor. The process describes the complete conversion of hydrocarbon (i.e., $CH_4$) and $CO_2$ reactants, in stream 1, within the permeable reformer A, to $H_2$ and CO products. The occurring reactions are (1),(2),(3) or (2),(3) only. Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with $H_2$ to be separated in permeate stream 1b via valve A1. Exiting from the permreactor, stream 2, containing only CO and non-permeating $H_2$, or CO, non-permeating $H_2$, and traces of unreacted steam, passes through heat exchanger B and moisture adsorbent C to remove unreacted steam and yield an all dry stream of $H_2$ and CO. Stream 8, of $H_2$ and CO (synthesis gas) enters into the methanol synthesis reactor D, wherein methanol is produced via the following exothermic reaction: $CO+2H_2=CH_3OH$, $\Delta H^{o}_{298}=-128.2kJ/mol$ (13.1). Reactor D, is a three phase slurry type reactor or a catalytic plug flow reactor with methanol to be produced in gas or liquid phase depending on the temperature, pressure and feed composition in the reactor and the type of catalyst used. Zinc, copper and chromium oxide catalysts are well known to convert synthesis gas to methanol. Methanol from stream 9 is fed to a methanol driven fuel cell for electric current generation. Optionally, stream 9 containing methanol enters into steam reforming reactor E for continuous catalytic methanol-steam reforming reaction in similar type catalysts. The reforming reaction in reactor E is as follows: $CH_3OH+H_2O=3H_2+CO_2$, $\Delta H^{o}_{298}=49.5kJ/mol$ (13.2). Exiting from the reactor E, gaseous stream 11, condenses unreacted steam and methanol in heat exchanger F, and the exit product gas through stream 14 is $H_2$ and $CO_2$. Steam in reactor E is provided through streams 6,10,13,20 which is generated by the heat exchanging process in heat exchangers B and F.

Pure $H_2$ and $CO_2$ mixture from exit stream 14, can be used as feed in molten carbonate fuel cells or in alternative methanol synthesis via the opposite reaction of methanol steam reforming, listed above. Optionally, bypass streams 15, 16 can be fed into stream 8 to add $CO_2$ and $H_2$ into the synthesis gas mixture fed into reactor D, to adjust its composition for increasing methanol production efficiency in the catalyst in reactor D via the reverse (13.2) reaction. Optionally also, stream 1c, which is a bypass stream of stream 1b and contains pure hydrogen, can be recycled into stream 8 via stream 16, for adjusting the hydrogen composition in this stream where necessary, to increase the efficiency of methanol synthesis in reactor D. Streams 15 and 1c merge into stream 16 via valve D1.

Hydrogen in stream 14 can be used as a mixture with $CO_2$, or as pure $H_2$ after the $CO_2$ condensation and removal.

Produced hydrogen from streams 1b and 14, can be used in applications mentioned already in embodiments described in Fig.6 and Fig.9. The $H_2$ and $CO_2$ mixture of stream 14 can be used in synthesis or fuel applications mentioned already in same embodiments. Reformers A and E are endothermic and flue gas streams 3,4 and 18,19 respectively are used to provide the necessary heat content to drive parallel reactions (1), (2), (3) and (13.2) respectively to completion. Streams 3 and 18 can be fed by a bypass stream of stream 2. Optionally, reformer A can be a non-permeable reformer with only one post-reaction outlet (exit), this of stream 2, which delivers all products and unreacted reactants into the heat exchanger B and next into reactor D.

We claim:

1. A reactor which is used as a steam and $CO_2$ hydrocarbon reforming, steam-alcohol reforming, water gas shift, and dehydrogenation reactor, which consists of a far-outer impermeable hollow tubular cylinder which nests two more concentric hydrogen permeable tubular cylinders, having the inner permeable one to be nested within the outer permeable, with the inner permeable cylinder to be filled with catalyst particles, with tubular type heaters to be located within the catalyst zone, and run parallel to the inner cylindrical axis, with the catalyst in pellet or particle form to be a reforming, water gas shift or dehydrogenation catalyst depending on the feedstocks fed in the inlet of the reactor and the type of reactions conducted within the catalytic zone, moreover, with hydrogen to be removed via permeation along the inner membrane tube, wherein the membrane is made by a metal, metal alloy, non-porous inorganic or carbon material, with carbon monoxide, carbon dioxide, steam, hydrocarbons, alcohols and non-permeate hydrogen to be rejected by the membrane and exit through the main outlet of the inner tube, with the permeate hydrogen to be diluted by a carrier gas flowing along the annulus between the inner and outer permeable tubes and to be further removed through permeation along the outer permeable membrane tube, wherein the outer membrane is made by a metal, non-porous inorganic, or carbon material, so that second permeated stream contains pure hydrogen only, with the annular space between the outer membrane tube and the far-outer impermeable tube which receives final permeate hydrogen to contain a selective catalyst, wherein permeate hydrogen reacts with a sweep component flowing through the inlet of this annular space, parallel to the outer membrane tube, in an exothermic type reaction, with the heat generated by the exothermic reaction in the most-outer catalytic zone to be transferred via the radial direction into the main catalytic reaction zone of the inner membrane tube thus providing for part of the heat load necessary to drive the endothermic catalytic reactions in the inner membrane tube, with the main heating load of this inner catalytic zone to be achieved via heat transfer from tubes flowing gas, arranged symmetrically around the reactor axis and operated in the combustion regime by flowing waste type hydrocarbons or hydrocarbon-hydrogen mixtures mixed with oxygen or air, also by flowing unreacted hydrocarbons and carbon monoxide post-reaction species, and any of their mixtures, exiting from the inner membrane tube outlet and recovered in the downstream of the reactor through various separation processes including separation through membrane permeation, and by having these mixtures to be recycled as fuel into the inlet of these heating tubes to support combustion and heat provision in the surrounding inner catalytic zone, with the sweep component, which reacts with the hydrogen permeated from the outer membrane tube, to be

an unsaturated hydrocarbon such as an alkene or alkyne for hydrogenation to a saturated hydrocarbon,

also to be carbon monoxide for hydrogenation to methanol or gasoline hydrocarbons,

also to be nitrogen for hydrogenation to ammonia,

also to be an aromatic hydrocarbon for reduction with hydrogen to a non-aromatic hydrocarbon,

also to be an unsaturated alcohol, phenol, aldehyde, ketone, or acid for reduction with hydrogen to a corresponding saturated component,

also to be an alkyl or aryl halide for reduction with hydrogen to a corresponding non-halogene component,

also to be a nitroalkane or aromatic nitro compound for reduction with hydrogen to a corresponding primary amine.

**2.** The reactor assembly and process of claim 1, wherein annular space enclosed between the outer permeable membrane tube and the far-outer impermeable metal tube is empty and the permeate pure hydrogen through outer membrane tube is used as feed in various consecutive applications including hydrogenation reactors for methanol, gasoline hydrocarbons and ammonia synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

**3.** The process of claim 1 wherein the inner membrane tube is made by a porous inorganic or inorganic-metal membrane material with hydrogen to permeate through the membrane, and carbon monoxide, carbon dioxide, steam, reactant and product hydrocarbons and alcohols to permeate also through the membrane in a lesser degree, with hydrogen only to permeate through the outer metal, non-porous inorganic or carbon membrane tube and with the remaining non-permeate species to exit through the reject outlet of the annular space created between the two membrane tubes either as it is mixture or after mixing with another carrier gas flowing through the same annular space, with the permeate pure hydrogen through the outer membrane to be used as feed in various consecutive applications including hydrogenation reactors for methanol, gasoline hydrocarbons and ammonia synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

**4.** The process of claim 1 as applied to carbon dioxide hydrocarbon reforming and dehydrogenation reactions, wherein the inner membrane tube is made by a porous inorganic or inorganic-metal material with hydrogen to permeate through the membrane, and carbon monoxide, carbon dioxide, reactant and product hydrocarbon species, to permeate also through the membrane in a lesser degree, and with the outer membrane tube to be made by an organic polymer membrane which withstands high temperatures and is permselective to both hydrogen and carbon dioxide species, with hydrogen and carbon dioxide in the reforming reaction case or hydrogen only in the dehydrogenation case to permeate through the outer membrane, and with the remaining non-permeate species to exit through the reject outlet of the annular space created between the two membrane tubes, either as it is mixture or after mixing with another carrier gas flowing through the same annular space, with the permeate through the outer membrane hydrogen and carbon dioxide mixture to be used for methanol synthesis and as feed in molten carbonate fuel cells, and in the corresponding case wherein hydrogen only is the permeate through the outer membrane tube, the permeate hydrogen to be used as feed in various consecutive applications including hydrogenation reactors for methanol, gasoline hydrocarbons and ammonia synthesis, also in gas turbines, engines, and fuel cells of

proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

5. A reactor which is used as a steam and $CO_2$ hydrocarbon reforming, steam-alcohol reforming, water gas shift, and dehydrogenation reactor, which consists of a most outer non-permeable tubular cylinder which is hollow in the center and nests two more concentric hollow membrane tubular cylinders, a next-inner one and a most-inner one, which are both made by permeable materials with the annular space between most-outer and next-inner cylinders to contain a metallic catalyst in the form of pellets or particles, with the catalyst to be a reforming, water gas shift or dehydrogenation catalyst depending on the feedstocks fed in the inlet of the annular catalytic zone and the type of reactions conducted within the catalytic zone, with the next-inner cylinder to nest also a concentric most-inner hollow membrane cylinder, with next-inner cylinder to be made by a metal, metal alloy, non-porous inorganic, or carbon material which is permeable only to hydrogen, with product hydrogen from the catalytic reaction zone to permeate through the lateral membrane surface of next-inner cylinder with carbon monoxide, carbon dioxide, steam, hydrocarbons, alcohols and non-permeate hydrogen to be rejected by the next-inner membrane and exit through outlet fitting ports located by the end of the catalytic zone, with permeate hydrogen flowing along the annular zone between next-inner and most-inner cylinders to be diluted by a carrier gas flowing along the same annulus and to be further removed via permeation across the most-inner permeable membrane tube, wherein most-inner membrane tube is made by metal, metal-alloy, non-porous inorganic or carbon materials, so that secondly permeated stream flowing inside most-inner membrane tube contains only pure hydrogen, with the most-inner membrane tube to contain a selective catalyst in form of particles or pellets, wherein permeate hydrogen reacts with a sweep component flowing through an inlet port of the most-inner membrane tube in an exothermic type reaction, with the heat generated by the exothermic reaction in the most-inner catalyst zone to be transferred into the main catalytic reaction zone enclosed between most-outer and next-inner hollow cylinders, thus providing for part of the heat load necessary to drive the endothermic catalytic reactions occurring in this zone, with the main heating of the overall cylindrical assembly and main catalytic zone to be achieved by heat transfer coming from combustion of gases, including combustion of waste type hydrocarbons and hydrocarbon-hydrogen mixtures mixed with oxygen or air, also of unreacted hydrocarbons and carbon monoxide post-reaction species and any of their mixtures exiting from the corresponding reaction outlet port, which are recovered in the downstream of the reactor through various separation processes including separation through membrane permeation and recycled as fuel flowing along the external side of the most-outer impermeable cylinder to support combustion and heat provision in enclosed main catalytic zone, with the sweep component which reacts with the hydrogen permeated in the most-inner membrane tube, to be

an unsaturated hydrocarbon such as an alkene or alkyne for hydrogenation to a saturated hydrocarbon,

also to be carbon monoxide for hydrogenation to methanol or gasoline hydrocarbons,

also to be nitrogen for hydrogenation to ammonia, also to be an aromatic hydrocarbon for reduction with hydrogen to a non-aromatic hydrocarbon,

also to be an unsaturated alcohol, phenol, aldehyde, ketone, or acid for reduction with hydrogen to a corresponding saturated component,

also to be an alkyl or aryl halide for reduction with hydrogen to a corresponding non-halogene component,

also to be a nitroalkane or aromatic nitro compound for reduction with hydrogen to a corresponding primary amine.

**6.** The reactor assembly and process of claim 5, wherein most inner membrane tube is empty and the pure permeate hydrogen within this tube is used as feed in various consecutive applications including hydrogenation reactors for methanol, gasoline hydrocarbons, and ammonia synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

**7.** The process of claim 5 wherein next-inner hollow cylinder is made by a porous inorganic or inorganic-metal membrane, with hydrogen to permeate through the membrane, and carbon monoxide, carbon dioxide, steam, reactant and product hydrocarbons, alçohols, to permeate also through the membrane in a lesser degree, with hydrogen only to permeate through the most-inner metal, metal alloy, non-porous inorganic, or carbon membrane tube and with the remaining non-permeate species, to exit through the reject outlet of the annular space created between the next-inner and most-inner cylinders, either as it is mixture or after mixing with another carrier gas flowing through the same annular space, with the permeate through the inner membrane tube, pure hydrogen product, to be used as feed in various consecutive applications including hydrogenation reactors for methanol, gasoline hydrocarbons and ammonia synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

**8.** The process of claim 7, as applied to carbon dioxide hydrocarbon reforming and dehydrogenation reactions only, wherein the most-inner membrane tube is made by an organic polymer membrane which withstands high temperatures and is permselective to both hydrogen and carbon dioxide species, which permeate through the most-inner membrane tube, with the remaining non-permeate species to exit through the reject outlet of the annular space created between the next-inner and most-inner membrane tubes, either as it is mixture or after mixing with another carrier gas flowing through the same annular space, with the permeate through the most-inner membrane tube hydrogen and carbon dioxide mixture to be used for methanol synthesis and as feed in molten carbonate fuel cells, and in corresponding case wherein hydrogen only permeates through the most-inner membrane tube, the permeate hydrogen to be used as feed in various consecutive applications including hydrogenation reactors for methanol, gasoline hydrocarbons and ammonia synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

9. A reactor which is used as a carbon dioxide hydrocarbon reforming and dehydrogenation reactor, which consists of multiple membrane tubes nested within an outer non-permeable hollow metal cylinder which also contains a catalyst in particle or pellet form, with the catalyst to be a reforming or dehydrogenation catalyst depending on the feedstocks fed in the inlet of the catalytic zone and the type of reactions conducted within the catalytic zone, with the multiple membrane tubes to be made by organic type polymer membrane material which withstands high temperature and is permselective to both hydrogen and carbon dioxide species which permeate into the multiple inner membrane tubes from the catalytic zone, with the remaining non-permeate carbon monoxide, product and reactant hydrocarbons and non-permeate hydrogen and carbon dioxide to be rejected by the polymer membrane tubes and exit through outlet fitting ports located by the end of the catalyst zone, with permeate hydrogen and carbon dioxide mixture from the reforming reaction or permeate hydrogen only from the dehydrogenation reaction, which are flowing in the inner side of the membrane tubes either as unmixed gas or as a mixture with another carrier component flowing through a common inlet via all the membrane tubes, to be continuously removed via a common impermeable metal shell which is interconnected with all the membrane tubes and sealed from the gases flowing out of the catalytic reaction zone of the outer cylinder, with the multiple organic polymer membrane tubes to contain a selective catalyst in form of particles or pellets wherein mixture of permeate hydrogen and carbon dioxide react to produce methanol or carbon monoxide or methane, and alternatively, permeate hydrogen only reacts with a sweep component flowing through all membrane tubes via a common inlet, in an exothermic type of reaction, with the heat generated by the exothermic reaction in the catalytic zone enclosed within the tubes to be transferred in the outer catalytic reaction zone, thus providing for part of the heat load necessary to drive the occurring endothermic reforming or dehydrogenation reactions, with the main heating of the outer cylinder and enclosed catalytic zone to be achieved via heat transfer from combustion of gas flowing in external side of the outer cylinder, including combustion of waste type hydrocarbons and hydrocarbon-hydrogen mixtures mixed with oxygen or air, including unreacted hydrocarbons and carbon monoxide post-reaction species and any of their mixtures exiting from the outer catalytic zone via suitable outlet fitting ports, which gases are recovered in the downstream of the reactor through various separation processes including separation through membrane permeation and recycled as fuel along the external side of the outer cylinder to support combustion and heat provision in the enclosed outer catalytic zone, with the sweep component which reacts with the hydrogen permeated in the inner membrane tubes, to be

an unsaturated hydrocarbon such as an alkene or alkyne for hydrogenation to a saturated hydrocarbon,

also to be carbon monoxide for hydrogenation to methanol or gasoline hydrocarbons,

also to be nitrogen for hydrogenation to ammonia,

also to be an aromatic hydrocarbon for reduction with hydrogen to a non-aromatic hydrocarbon,

also to be an unsaturated alcohol, phenol, aldehyde, ketone, or acid for reduction with hydrogen to a corresponding saturated component,

also to be an alkyl or aryl halide for reduction with hydrogen to a corresponding non-halogene component,

also to be a nitroalkane or aromatic nitro compound for reduction with hydrogen to a corresponding primary amine.

**10.** The reactor assembly and process of claim 9, wherein the inner membrane tubes are empty and the hydrogen and carbon dioxide mixture or the hydrogen gas only which permeate in these tubes and recovered in the downstream is used as feed in various consecutive applications including hydrogenation reactors for methanol, gasoline hydrocarbons and ammonia synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

**11.** The process of claim 1, as applies to the steam and $CO_2$ hydrocarbon reforming reactions, with $H_2$ and CO to be produced via the reversible hydrocarbon steam reforming, hydrocarbon $CO_2$ reforming, and water gas shift reactions, with the final permeate stream to contain pure hydrogen product, permeated through the far outer membrane tube, and with the reject exit stream from the reactor which contain carbon monoxide product, non-permeate hydrogen product, unreacted hydrocarbon, carbon dioxide and unreacted and produced steam to be passed through a heat exchanger to reduce its temperature and condense the containing steam by generating new steam in other side of the exchanger which is used as feed into the first reforming reactor and any subsequently placed steam reforming reactor, with the exit stream from the heat exchanger to be passed through a bed of moisture adsorbing particles to remove any moisture content, with the dry cooled exit gas mixture to enter into a membrane permeator made by one of the following materials:

organic polymer membrane,
inorganic membrane,
composite inorganic-metal-organic membrane,
composite organic-inorganic membrane,
composite organic-metal membrane,

which all materials are permselective to $H_2$ and $CO_2$ and separate these two species in permeate stream from the unreacted hydrocarbon and carbon monoxide product which exit from the non-permeate side of the permeator as a reject stream, with the $H_2$ and $CO_2$ permeate product mixture to be used for methanol synthesis and as feed in molten carbonate fuel cells, also in other

chemical synthesis
and fuel type reactions

either as a mixture or after the $CO_2$ condensation and removal, as pure hydrogen, either

as single hydrogen stream or

as combined hydrogen stream after its combination with the hydrogen stream permeated from the first permeable reactor.

**12.** The process of claim 5, as applies to the steam and $CO_2$ hydrocarbon reforming reactions, with $H_2$ and CO to be produced via the reversible hydrocarbon steam reforming, hydrocarbon $CO_2$ reforming, and water gas shift reactions, with the final permeate stream to contain pure hydrogen product, permeated through the most inner membrane tube, and with the reject exit stream from the reactor which contains carbon monoxide and non-permeate hydrogen product, unreacted hydrocarbon, carbon dioxide and unreacted and produced steam to be passed through a heat exchanger to reduce its temperature and condense the containing steam by generating new steam in other side of the exchanger which is used as feed into the first reforming reactor and any subsequently placed steam reforming reactor, with the exit stream from the heat exchanger to be passed through a bed of moisture adsorbing particles to remove any moisture content, with the dry cooled exit gas mixture to enter into a membrane permeator made by one of the following materials:

organic polymer membrane,
inorganic membrane
composite inorganic-metal-organic membrane,
composite organic-inorganic membrane,
composite organic-metal membrane,

which all materials are permselective to $H_2$ and $CO_2$ and separate these two species in permeate stream from the unreacted hydrocarbon and carbon monoxide product which exit from the non-permeate side of the permeator as a reject stream, with the $H_2$ and $CO_2$ permeate product mixture to be used for methanol synthesis and as feed in molten carbonate fuel cells, also in other

chemical synthesis
and fuel type reactions

either as a mixture or after the $CO_2$ condensation and removal, as pure hydrogen, either

as single hydrogen stream or
as combined hydrogen stream after its combination with the hydrogen stream permeated from the first permeable reactor.

**13.** The process of claim 9, as applies to the $CO_2$ hydrocarbon reforming reaction, by feeding $CO_2$ and a hydrocarbon or $CO_2$ and a mixture of hydrocarbons in the catalytic reaction zone, with $H_2$ and CO to be produced via the reversible hydrocarbon $CO_2$ reforming and water gas shift reactions, with the final permeate stream to contain hydrogen product, carbon dioxide reactant and traces of steam which may also permeate through the multiple inner polymer membrane tubes, with the steam to be removed by passing the stream through a bed of moisture adsorbing particles, with the remaining hydrogen and $CO_2$ mixture to be used in consecutive applications, and with the reject exit stream from the reactor which contains carbon monoxide product, non-permeate hydrogen product, non-permeate unreacted carbon dioxide, unreacted hydrocarbon and traces of product steam to be passed through a bed of moisture adsorbing particles to remove any moisture content, with the dry cooled exit gas mixture to enter into a membrane permeator made by one of the following materials:

organic polymer membrane,
inorganic membrane

composite inorganic-metal-organic membrane,
composite organic-inorganic membrane,
composite organic-metal membrane,

which all materials are permselective to $H_2$ and $CO_2$ and separate these two species in permeate stream from the unreacted hydrocarbon and carbon monoxide product which exit from the non-permeate side of the permeator as a reject stream, with the $H_2$ and $CO_2$ permeate product mixture to be used for methanol synthesis and as feed in molten carbonate fuel cells, also in other

chemical synthesis
and fuel type reactions

either as single stream or as combined stream after its combination with the hydrogen and $CO_2$ stream permeated from the first permeable reactor.

**14.** The process of claim 12, wherein the membrane permeator which follows the permeable reforming reactor is made by a metal, metal alloy, non-porous inorganic, or carbon membrane which is permselective only to hydrogen and separate hydrogen in permeate stream from the unreacted hydrocarbon, carbon dioxide, and product carbon monoxide, which all exit from the non-permeate side of the permeator as a reject stream, with the recovered hydrogen in permeate stream to be used either directly, or after combination with the permeate hydrogen recovered from the first permeable reactor, in

chemical synthesis, including methanol, gasoline hydrocarbons and ammonia,
in fuel type reactions

including as hydrogen feed, in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

**15.** The process of claim 12, with the reject stream from the permeator containing unreacted hydrocarbon and CO to enter into a consecutively placed steam reformer to react with steam over a bed of metallic catalyst via the steam reforming and water gas shift reactions and be converted into $H_2$ and $CO_2$ products, having this exit stream from last reformer to condense its unreacted steam by passage through a heat exchanger and by generating new steam in other side of the heat exchanger which is used as feed in the inlet of this last reformer, having the final exit dry mixture of $H_2$ and $CO_2$ from the heat exchanger to be combined with the permeate from the membrane permeator $H_2$ and $CO_2$ stream, to make one combined stream of $H_2$ and $CO_2$ to be used for methanol synthesis and as feed in molten carbonate fuel cells, also in other

chemical synthesis
and fuel type reactions

either as a mixture or after the $CO_2$ condensation and removal, as pure hydrogen, either

as single hydrogen stream or
as combined hydrogen stream after its combination with the hydrogen stream permeated from the first permeable reactor.

**16.** The process of claim 14, with the reject stream from the permeator containing

unreacted hydrocarbon, carbon dioxide and carbon monoxide product to enter into a consecutively placed steam and carbon dioxide reformer to react with steam and carbon dioxide over a bed of metallic catalyst via the reversible reactions of hydrocarbon-steam reforming, hydrocarbon-carbon dioxide reforming, and water gas shift, and be converted into $H_2$, CO and $CO_2$ products, having this exit stream from last reformer to condense its unreacted steam by passage through a heat exchanger and by generating new steam in other side of the heat exchanger which is used as feed in the inlet of this last reformer, having the final exit dry mixture of $H_2$, CO and $CO_2$ from the heat exchanger to be used for

chemical synthesis,
and as fuel

either as it is mixture, or after the $CO_2$ condensation and removal, as pure synthesis gas mixture of hydrogen and carbon monoxide, either

as single stream or
as combined stream

after its combination with the hydrogen stream permeated from the permeator and the first permeable reforming reactor.

**17.** The process of claim 12 wherein the hydrocarbon is a single constituent or a mixture of constituents of the following components:

methane,
ethane,
propane,
n-butane,
i-butane,
methanol,
ethanol,
propanol,
butanol,
natural gas rich in methane,
coal gas rich in methane,
landfill gas rich in methane,
flue gas rich in methane,

and wherein the combined hydrocarbon and carbon dioxide gas mixture is substituted by:

a $CH_4$ and $CO_2$ mixture,
acidic natural gas rich in $CH_4$ and $CO_2$,
coal gas rich in $CH_4$ and $CO_2$,
landfill gas rich in $CH_4$ and $CO_2$,
other refinery and flue gas mixtures rich in $CH_4$ and $CO_2$.

**18.** The process of claim 12 wherein the membrane in permeator is made from an organic polymer or composite or copolymer of organic polymers selected from the group of

polyimides,
polycarbonates,

polysulfones,
polybenziimidazoles,
polyphosphazenes,
polyamides,
polystyrenes,
polycaprolactams,
parylenes,
polyvinyl halides,
polyacetates,
polysiloxanes

or from inorganic-organic composite materials made by a mixture of one or more of the above polymers with one or more of the following ceramic oxides:

alumina ($Al_2O_3$),
titania ($TiO_2$),
silica ($SiO_2$),
zirconia ($ZrO_2$).

**19.** The process of claim 9 wherein the inner membrane tubes within the reactor are made from an organic polymer or composite or copolymer of organic polymers selected from the group of

polyimides,
polycarbonates,
polysulfones,
polybenziimidazoles,
polyphosphazenes,
polyamides,
polystyrenes,
polycaprolactams,
parylenes,
polyvinyl halides,
polyacetates,
polysiloxanes.

**20.** The process of claim 12 wherein the permeator following the first permreactor is replaced by a catalytic permreactor to reactively process the exit stream from the first permreactor which is rich in CO product, by conducting the water gas shift reaction with $H_2$ and $CO_2$ products, also in case of low conversion in the first permreactor wherein first permreactor exit stream contains significant amounts of unreacted methane and carbon dioxide by conducting as well in following catalytic permreactor the reversible methane steam reforming and methane carbon dioxide reforming reactions together with the water gas shift reaction over a bed of metallic catalyst with main products $H_2$, CO and with the following membrane permreactor to be made by one of the following materials:

metal or metal alloy membrane,
non-porous inorganic membrane,
carbon membrane

which all materials are permselective to $H_2$ and separate $H_2$ only in permeate stream of the permreactor from the unreacted hydrocarbon, steam, $CO_2$, and CO which all exit from the non-permeate side of the permreactor as a reject stream which is recycled as feed into the first permreactor if it is rich in $CO_2$, or in the second permreactor if it is rich in CO, with the permeate $H_2$ to be used in

chemical synthesis

and fuel type reactions

either , as single hydrogen stream or

as combined hydrogen stream after its combination with the hydrogen stream permeated from the first permeable reactor.

**21.** The process of claim 11 wherein the permeator following the first permreactor is replaced by a catalytic permreactor to reactively process the exit stream from the first permreactor which is rich in CO product, by conducting the water gas shift reaction with $H_2$ and $CO_2$ products, also in case of low conversion in the first permreactor wherein first permreactor exit stream contains significant amounts of unreacted methane and carbon dioxide by conducting as well in following catalytic permreactor the reversible methane steam reforming and methane carbon dioxide reforming reactions together with the water gas shift reaction over a bed of metallic catalyst with main products $H_2$, CO and with the following membrane permreactor to be made by one of the following materials:

metal or metal alloy membrane,

non-porous inorganic membrane,

carbon membrane

which all materials are permselective to $H_2$ and separate $H_2$ only in permeate stream of the permreactor from the unreacted hydrocarbon, steam, $CO_2$, and CO which all exit from the non-permeate side of the permreactor as a reject stream which is recycled as feed into the first permreactor if it is rich in $CO_2$, or in the second permreactor if it is rich in CO, with the permeate $H_2$ to be used in

chemical synthesis

and fuel type reactions

either , as single hydrogen stream or

as combined hydrogen stream after its combination with the hydrogen stream permeated from the first permeable reactor.

**22.** The process of claim 12 wherein the feed stream into first permreactor consists of a hydrocarbon and carbon dioxide or a mixture of hydrocarbons and carbon dioxide, reformed over a bed of metallic catalyst via the reversible $CO_2$ hydrocarbon reforming and water gas shift reactions to produce $H_2$ and CO products.

**23.** The process of claim 11 wherein the feed stream into first permreactor consists of a hydrocarbon and carbon dioxide or a mixture of hydrocarbons and carbon dioxide, reformed over a a bed of metallic catalyst via the reversible $CO_2$ hydrocarbon reforming and water gas shift reactions to produce $H_2$ and CO products.

**24.** The process of claim 12 wherein the combined $H_2$ and $CO_2$ product mixture from the permeator is used:

(a) for direct methanol synthesis via the reaction: $CO_2+3H_2=CH_3OH+H_2O$,

(b) for direct feed in molten carbonate fuel cell (MCFC) units for electricity generation via the overall electrochemical reaction: $H_2+CO_2+1/2O_2$(cathode) --- $H_2O+CO_2$(anode),

(c) for other $CO_2$ and $H_2$ direct combination reaction,

moreover, after the removal of $CO_2$ by condensation, the generated pure $H_2$ is combined with pure $H_2$ coming out of the first reforming reactor and used:

(d) as fuel feed in hydrogen based fuel cell units including molten carbonate, solid oxide, proton exchange, alkaline, phosphoric type,

(e) as fuel feed in gas turbines, conventional and jet type gas engines,

(f) as synthesis reactant in consecutive hydrogenation reactors including these for methanol, ammonia and gasoline hydrocarbon synthesis, also these for saturation of unsaturated hydrocarbons including alkenes to alkanes, alkynes to alkenes to alkanes, also these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides, and these for reduction of nitroalkanes and aromatic nitro compounds into corresponding primary amines.

**25** The process of claim 11 wherein the combined $H_2$ and $CO_2$ product mixture from the permeator is used:

(a) for direct methanol synthesis via the reaction: $CO_2+3H_2=CH_3OH+H_2O$,

(b) for direct feed in molten carbonate fuel cell (MCFC) units for electricity generation via the overall electrochemical reaction: $H_2+CO_2+1/2O_2$(cathode) --- $H_2O+CO_2$(anode),

(c) for other $CO_2$ and $H_2$ direct combination reaction,

moreover, after the removal of $CO_2$ by condensation, the generated pure $H_2$ is combined with pure $H_2$ coming out of the first reforming permreactor and used:

(d) as fuel feed in hydrogen based fuel cell units including molten carbonate, solid oxide, proton exchange, alkaline, phosphoric type,

(e) as fuel feed in gas turbines, conventional and jet type gas engines,

(f) as synthesis reactant in consecutive hydrogenation reactors including these for methanol, ammonia and gasoline hydrocarbon synthesis, also these for saturation of unsaturated hydrocarbons including alkenes to alkanes, alkynes to alkenes to alkanes, also these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides, and these for reduction of nitroalkanes and aromatic nitro compounds into corresponding primary amines.

**26.** The process of claim 12 wherein the feed stream into the first permreactor consists only of carbon monoxide and steam ($H_2O(g)$) mixture, reacting over a bed of metallic catalyst to produce $H_2$ and $CO_2$ via the water gas shift reaction alone, with hydrogen to permeate through the most-inner membrane tubes and with the remaining

components including unreacted carbon monoxide, steam, carbon dioxide product and non-permeate hydrogen to exit through the reject stream of the outer cylinder.

**27.** The process of claim 26 with the reject stream from the permeator containing non-permeate unreacted CO to be recycled into the inlet of first water gas shift permreactor for continuous water gas shift reaction into the main outer catalytic zone.

**28.** The process of claim 26 with the reject stream from the permeator containing non-permeate unreacted CO to enter into a consecutive placed water gas shift reactor to react with steam over a bed of metallic catalyst via the water gas shift reaction and be converted into $H_2$ and $CO_2$ product, having the exit stream from last shift reactor to condense its unreacted steam by passage through a heat exchanger and by generating new steam in the other side of the heat exchanger to be used as feed in the inlet of this last shift reactor in an autothermic type operation, having the final exit dry mixture of $H_2$ and $CO_2$ from last heat exchanger to be combined with the permeate from the membrane permeator $H_2$ and $CO_2$ stream, to make a combined stream for use as feed in methanol synthesis and molten carbonate fuel cells, also in other

chemical synthesis

and fuel type reactions

either as it is mixture or after the $CO_2$ condensation and removal, as pure hydrogen, either

as single hydrogen stream or

as combined hydrogen stream after its combination with the hydrogen stream permeated from the first permeable reactor.

**29.** The process of claim 5, as applies to dehydrogenation reactions of alkanes, with the feed to consist of pure or mixture of alkanes which are saturated hydrocarbons and react in the catalytic zone of the permreactor, with hydrogen and unsaturated alkenes to be produced via reversible dehydrogenation reactions, with the final permeate stream to contain pure hydrogen product permeated through the most-inner membrane tube and with the exit reject stream from the permreactor which contains product alkenes and non-permeate hydrogen and unreacted alkanes, to be passed through a heat exchanger to reduce its temperature by generating steam in other side of the exchanger which is used as feed into any steam requiring process with the exit from the heat exchanger alkenes, alkanes and hydrogen mixture to be entered into a membrane permeator wherein the membrane is made by one of the following materials:

organic polymer membrane,
inorganic membrane,
composite inorganic-metal-organic membrane
composite inorganic-organic membrane
composite metal-organic membrane
metal or metal alloy membrane
non-porous inorganic membrane
carbon membrane

which all materials are permselective to hydrogen only, and separate hydrogen in permeate stream from the unreacted alkanes and product alkenes, which exit from the non-permeate side of the permeator as a reject stream to be used for

polyolefin synthesis in consecutive polymerization reactors,

oxygenated compound synthesis in consecutive synthesis reactors,

including ethylene glycol, ethylene oxide, propylene glycol, propylene oxide, ethanol, propanol, isopropanol, with the hydrogen product recovered in the permeate stream of the permeator to be used as single hydrogen stream or as combined hydrogen stream after its combination with the hydrogen stream permeated through the first permeable reactor, in

chemical synthesis,

and in fuel type reactions,

including use as feedstock to hydrogenation reactors for methanol, ammonia, and gasoline hydrocarbon synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

**30.** The process of claim 1, as applies to dehydrogenation reactions of alkanes, with the feed to consist of pure or mixture of alkanes which are saturated hydrocarbons and react in the catalytic zone of the permreactor, with hydrogen and unsaturated alkenes to be produced via reversible dehydrogenation reactions, with the final permeate stream to contain pure hydrogen product permeated through the outer membrane tube and with the exit reject stream from the permreactor which contains product alkenes and non-permeate hydrogen and unreacted alkanes, to be passed through a heat exchanger to reduce its temperature by generating steam in other side of the exchanger which is used as feed into any steam requiring process with the exit from the heat exchanger alkenes, alkanes and hydrogen mixture to be entered into a membrane permeator wherein the membrane is made by one of the following materials:

organic polymer membrane,

inorganic membrane,

composite inorganic-metal-organic membrane

composite inorganic-organic membrane

composite metal-organic membrane

metal or metal alloy membrane

non-porous inorganic membrane

carbon membrane

which all materials are permselective to hydrogen only, and separate hydrogen in permeate stream from the unreacted alkanes and product alkenes, which exit from the non-permeate side of the permeator as a reject stream to be used for

polyolefin synthesis in consecutive polymerization reactors,

oxygenated compound synthesis in consecutive synthesis reactors,

including ethylene glycol, ethylene oxide, propylene glycol, propylene oxide, ethanol, propanol, isopropanol, with the hydrogen product recovered in the permeate stream of the permeator to be used as single hydrogen stream or as combined hydrogen stream after its combination with the hydrogen stream permeated through the first permeable reactor, in

chemical synthesis,

and in fuel type reactions,

including use as feedstock to hydrogenation reactors for methanol, ammonia, and gasoline hydrocarbon synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

**31.** The process of claim 9, as applies to dehydrogenation reactions of alkanes, with the feed to consist of pure or mixture of alkanes which are saturated hydrocarbons and react in the catalytic zone of the permreactor, with hydrogen and unsaturated alkenes to be produced via reversible dehydrogenation reactions, with the final permeate stream to contain pure hydrogen product permeated through the multiple inner polymer membrane tubes, and with the exit reject stream from the permreactor which contains alkenes and non-permeate hydrogen as products and unreacted alkanes, to be passed through a heat exchanger to reduce its temperature by generating steam in other side of the exchanger which is used as feed into any steam requiring process with the exit from the heat exchanger alkenes, alkanes and hydrogen mixture to be entered into a membrane permeator wherein the membrane is made by one of the following materials:

organic polymer membrane,

inorganic membrane,

composite inorganic-metal-organic membrane

composite inorganic-organic membrane

composite metal-organic membrane

metal or metal alloy membrane

non-porous inorganic membrane

carbon membrane

which all materials are permselective to hydrogen only, and separate hydrogen in permeate stream from the unreacted alkanes and product alkenes, which exit from the non-permeate side of the permeator as a reject stream to be used for

polyolefin synthesis in consecutive polymerization reactors,

oxygenated compound synthesis in consecutive synthesis reactors,

including ethylene glycol, ethylene oxide, propylene glycol, propylene oxide, ethanol, propanol, isopropanol, with the hydrogen product recovered in the permeate stream of the permeator to be used as single hydrogen stream or as combined hydrogen stream after its combination with the hydrogen stream permeated through the first permeable reactor, in

chemical synthesis,

and in fuel type reactions,

including use as feedstock to hydrogenation reactors for methanol, ammonia, and gasoline hydrocarbon synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

**32.** The process of claim 29 wherein the alkane hydrocarbon is a single constituent or a mixture of constituents of the following components:

ethane,

propane,

n-butane,
i-butane,
natural gas rich in ethane
natural gas rich in propane
refinery gas rich in ethane
refinery gas rich in propane
refinery gas rich in butane
refinery gas rich in isobutane
refinery gas rich in ethane, propane, butane, isobutane.

**33.** The process of claim 29 wherein the membrane in permeator is made from an organic polymer or composite or copolymer of organic polymers selected from the group of

polyimides,
polycarbonates,
polysulfones,
polybenziimidazoles,
polyphosphazenes,
polyamides,
polystyrenes,
polycaprolactams,
parylenes,
polyvinyl halides,
polyacetates,
polysiloxanes

or from inorganic-organic composite materials made by a mixture of one or more of the above polymers with one or more of the following ceramic oxides:

alumina ($Al_2O_3$),
titania ($TiO_2$),
silica ($SiO_2$),
zirconia ($ZrO_2$)

or from metal and metal alloys materials comprising by one or more of the following metals:

Palladium (Pd),
Vanadium (V),
Platinum (Pt),
Silver (Ag),
Chromium (Cr),
Copper (Cu),
Iron (Fe),
Nickel (Ni).

**34.** The process of claim 12 wherein the feed stream into the first permreactor consists only of a hydrocarbon and steam ($H_2O(g)$) mixture or an alcohol and steam mixture, reacting over a bed of metallic catalyst to produce $H_2$, $CO_2$ and traces of CO via

the reversible hydrocarbon steam reforming and water gas shift reactions, or alcohol steam reforming and water gas shift reactions, with hydrogen to permeate through the most-inner metal membrane tube and with the remaining components including unreacted hydrocarbons, alcohols, steam, carbon dioxide, carbon monoxide, and non-permeate hydrogen to exit through the reject stream of the outer cylinder.

**35.** The process of claim 34 with the reject stream from the permeator containing non-permeate unreacted hydrocarbons and product CO or unreacted alcohols and CO to be recycled into the inlet of first permeable reformer for continuous hydrocarbon-steam reforming and water gas shift reactions or alcohol steam reforming reactions into the catalytic zone of the outer cylinder.

**36.** The process of claim 34 with the reject stream from the permeator containing non permeate unreacted hydrocarbons and CO or alcohols and CO to enter into a consecutive placed reformer to react with steam over a bed of metallic catalyst via the steam reforming and water gas shift reactions and be converted into $H_2$, $CO_2$ product mixture, having the exit stream from last reforming reactor to condense its unreacted steam by passage through a heat exchanger and by generating new steam in other side of the heat exchanger to be used as feed in the inlet of the last reformer in an autothermic type operation, having the final exit dry mixture of $H_2$ and $CO_2$ from last heat exchanger to be combined with the permeate from the membrane permeator $H_2$ and $CO_2$ stream, to make a combined stream for use as feed in a methanol synthesis reactor and molten carbonate fuel cell unit, also in other

chemical synthesis

and fuel type reactions

either as it is mixture or after the $CO_2$ condensation and removal, as pure hydrogen, either

as a single hydrogen stream or

as combined hydrogen stream after its combination with the hydrogen stream permeated from the first permeable reforming reactor.

**37.** The process of claim 12 wherein the membrane permeator following the permeable reformer is replaced by a cryogenic separator, which operates at a cryogenic subzero temperature of absolute value higher than the condensation temperature of the unreacted steam, hydrocarbons, carbon dioxide, and lower than the condensation temperature of carbon monoxide and hydrogen, with the hydrogen and carbon monoxide gases to be separated as gases from the cryogenic separator, and with the steam, hydrocarbons and carbon dioxide to be separated as condensed liquids, with these liquified components to be continuously or periodically reheated by use of an immersed or surrounding heater to the section of the separator containing the liquified phase, and to be exited from the separator by use of a special valve, and be recycled into the inlet of the reforming reactor for continuous steam and carbon dioxide reforming and water gas shift reaction in the reformer, with the separated hydrogen and carbon monoxide mixture from the cryogenic separator to be used in following applications

methanol synthesis,

gasoline synthesis via Fischer-Tropsch synthesis route,
as combustion fuel in gas turbines and gas engines,
as fuel in solid oxide fuel cells,

either as is mixture, or after mixing with all or part of the hydrogen stream permeated from the permeable reformer.

**38.** The process of claim 22 wherein the membrane permeator following the permeable reformer is replaced by a cryogenic separator, which operates at a cryogenic subzero temperature of absolute value higher than the condensation temperature of the steam, hydrocarbons, carbon dioxide, and lower than the condensation temperature of carbon monoxide and hydrogen, with the hydrogen and carbon monoxide gases to be separated as gases from the cryogenic separator, and with the steam, hydrocarbons and carbon dioxide to be separated as condensed liquids, with these liquified components to be continuously or periodically reheated by use of an immersed or surrounding heater to the section of the separator containing the liquified phase, and to be exited from the separator by use of a special valve, and be recycled into the inlet of the reforming reactor for continuous steam and carbon dioxide reforming and water gas shift reaction in the reformer, with the separated hydrogen and carbon monoxide mixture from the cryogenic separator to be used in following applications

methanol synthesis,
gasoline synthesis via Fischer-Tropsch synthesis route,
as combustion fuel in gas turbines and gas engines,
as fuel in solid oxide fuel cells,

either as is mixture, or after mixing with all or part of the hydrogen stream permeated from the permeable reformer.

**39.** The process of claim 11 wherein the membrane permeator following the permeable reformer is replaced by a cryogenic separator, which operates at a cryogenic subzero temperature of absolute value higher than the condensation temperature of the unreacted steam, hydrocarbons, carbon dioxide, and lower than the condensation temperature of carbon monoxide and hydrogen, with the hydrogen and carbon monoxide gases to be separated as gases from the cryogenic separator, and with the steam, hydrocarbons and carbon dioxide to be separated as condensed liquids, with these liquified components to be continuously reheated by use of an immersed or surrounding heater to the section of the separator containing the liquified phase, and to be exited from the separator by use of a special valve, and be entered into the inlet of a consecutive reforming reactor for continuous steam and carbon dioxide reforming and water gas shift reaction in the reformer and conversion into $H_2$ and $CO_2$ products, having the exit stream from the last reforming reactor to condense its unreacted steam by passage through a heat exchanger and by generating new steam in the other side of the heat exchanger to be used as additional steam feed in the inlet of this last reforming reactor in an autothermic type operation, having the final exit dry mixture of $H_2$ and $CO_2$ from last heat exchanger to be used as direct feed in a methanol synthesis reactor and molten carbonate fuel cell unit, also in other

chemical synthesis

and fuel type reactions

either as it is mixture or after the $CO_2$ condensation and removal, as pure hydrogen, moreover with the separated hydrogen and carbon monoxide mixture from the cryogenic separator to be used in following applications,

methanol synthesis,

gasoline synthesis via Fischer-Tropsch synthesis route,

as combustion fuel in gas turbines and gas engines,

as fuel in solid oxide fuel cells,

either as is mixture, or after mixing with part or all of the hydrogen stream permeated from the first permeable reformer.

**40.** The process of claim 5 as applied to the carbon dioxide and steam reforming of hydrocarbons or carbon dioxide only reforming of hydrocarbons, wherein complete conversion of hydrocarbons and carbon dioxide occurs in the permeable reformer and the reject exit stream from the reformer consists only of hydrogen and carbon monoxide products and unreacted and produced steam, which exit reject stream enters as a fuel feed in a solid oxide fuel cell unit for electric current generation, with part or all of the permeate hydrogen out of the permreactor to be recycled into the reject stream to complement for hydrogen fuel entering into the fuel cell.

**41.** The process of claim 1 as applied to the carbon dioxide and steam reforming of hydrocarbons or carbon dioxide only reforming of hydrocarbons, wherein complete conversion of hydrocarbons and carbon dioxide occurs in the permeable reformer and the reject exit stream from the reformer consists only of hydrogen and carbon monoxide products and unreacted and produced steam, which exit reject stream enters as a fuel feed in a solid oxide fuel cell unit for electric current generation, with part or all of the permeate hydrogen out of the permreactor to be recycled into the reject stream to complement for hydrogen fuel entering into the fuel cell.

**42.** The process of claim 5 as applied to the carbon dioxide and steam reforming of hydrocarbons or carbon dioxide reforming of hydrocarbons, wherein complete conversion of hydrocarbons and carbon dioxide occurs in the permeable reformer and the reject exit stream from the reformer consists only of hydrogen and carbon monoxide products and unreacted and produced steam, which stream enters into a heat exchanger to reduce its temperature and condense the containing steam by generating new steam in other side of the exchanger which is used as feed into the first reforming reactor and any subsequently placed steam reforming or water gas shift reactor, with the exit stream from the heat exchanger to be passed through a bed of moisture adsorbing particles to remove any moisture content, with the dry cooled exit gas mixture to enter into a membrane permeator made by one of the following materials:

organic polymer membrane,

inorganic membrane

composite inorganic-metal-organic membrane,

composite organic-inorganic membrane,

composite organic-metal membrane,

metal or mtal-alloy membrane,
non-porous inorganic membrane,
carbon membrane,

which all materials are permselective to hydrogen, and separate hydrogen in permeate stream from carbon monoxide product which exit from the non-permeate side of the permeator as a reject stream, with the separated hydrogen gas from the permeator and the permeable reforming reactor to be used in

chemical synthesis
and fuel type reactions

including hydrogen feed in hydrogenation reactors for methanol, ammonia and gasoline hydrocarbon synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types, and with the rejected CO containing stream from the permeator to be used in

methanol and gasoline hydrocarbons synthesis,
as fuel feed in solid oxide fuel cells,
as feed in a consecutive water gas shift reactor for production of $H_2$ and $CO_2$.

**43.** The process of claim 5 as applied to the carbon dioxide and steam reforming of hydrocarbons or carbon dioxide only reforming of hydrocarbons, wherein high enough conversion of hydrocarbons and carbon dioxide occurs in the permeable reformer, so that reject exit stream from the reformer contains non-permeate hydrogen product, carbon monoxide product, traces of unreacted hydrocarbons and carbon dioxide, and unreacted and produced steam, which stream enters into a heat exchanger to reduce its temperature and condense the containing steam by generating new steam in other side of the exchanger which is used as feed into the first reforming reactor and any subsequently placed steam reforming or water gas shift reactor, with the exit stream from the heat exchanger to be passed through a bed of moisture adsorbing particles to remove any moisture content, with the dry exit gas mixture to enter into a methanol synthesis catalytic reactor which produces methanol in the gas or liquid phase by reacting hydrogen and carbon monoxide over a metallic catalyst, with the methanol product stream to exit from the synthesis reactor and with a part or all of it to be used as fuel feed in a methanol driven fuel cell, also with a part of it to be fed in a consecutive methanol steam reforming catalytic reactor wherein methanol reacts with steam over a bed of metallic catalyst via the methanol decomposition reaction to hydrogen and carbon monoxide and the parallel water gas shift reaction to hydrogen and carbon dioxide, with final reaction products to be hydrogen and carbon dioxide which together with unreacted steam exit from the last methanol steam reforming reactor and passes through a heat exchanger to condense the containing steam by generating new steam in other side of the exchanger which is used as feed into the two reforming reactors, with the exit stream from the heat exchanger to contain only hydrogen and carbon dioxide which is used as feed in molten carbonate fuel cells, or after the $CO_2$ condensation and removal, pure hydrogen is recovered and used as feed in hydrogenation reactors for methanol, ammonia and gasoline hydrocarbon synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

**44.** The process of claim 1 as applied to the carbon dioxide and steam reforming of hydrocarbons or carbon dioxide only reforming of hydrocarbons, wherein high enough conversion of hydrocarbons and carbon dioxide occurs in the permeable reformer, so that reject exit stream from the reformer contains non-permeate hydrogen product, carbon monoxide product, traces of unreacted hydrocarbons and carbon dioxide, and unreacted and produced steam, which stream enters into a heat exchanger to reduce its temperature and condense the containing steam by generating new steam in other side of the exchanger which is used as feed into the first reforming reactor and any subsequently placed steam reforming or water gas shift reactor, with the exit stream from the heat exchanger to be passed through a bed of moisture adsorbing particles to remove any moisture content, with the dry exit gas mixture to enter into a methanol synthesis catalytic reactor which produces methanol in the gas or liquid phase by reacting hydrogen and carbon monoxide over a metallic catalyst, with the methanol product stream to exit from the synthesis reactor and with a part or all of it to be used as fuel feed in a methanol driven fuel cell, also with a part of it to be fed in a consecutive methanol steam reforming catalytic reactor wherein methanol reacts with steam over a bed of metallic catalyst via the methanol decomposition reaction to hydrogen and carbon monoxide and the parallel water gas shift reaction to hydrogen and carbon dioxide, with final reaction products to be hydrogen and carbon dioxide which together with unreacted steam exit from the last methanol steam reforming reactor and passes through a heat exchanger to condense the containing steam by generating new steam in other side of the exchanger which is used as feed into the two reforming reactors, with the exit stream from the heat exchanger to contain only hydrogen and carbon dioxide which is used as feed in molten carbonate fuel cells, or after the $CO_2$ condensation and removal, pure hydrogen is recovered and used as feed in hydrogenation reactors for methanol, ammonia and gasoline hydrocarbon synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

**45.** The process of claim 43 wherein a part or all of the product stream of hydrogen and carbon dioxide mixture exiting from the last methanol steam reforming reactor is recycled as side feed into the methanol synthesis reactor, and wherein a part or all of the permeate hydrogen stream coming out of the first permeable reformer is recycled as well as side feed into the methanol synthesis reactor, so that a combined mixture of hydrogen, carbon monoxide and carbon dioxide is used within this catalytic reactor for increasing the efficiency of methanol synthesis.

## Abstract of the Disclosure

Overall permreactor-separator process designs and effective permreactor designs with increased mass and heat transfer, reactant conversion, product yield and optional recycling for processing methane, hydrocarbons, alcohols, carbon monoxide, natural gas, acidic natural gas, coal gas, biomass gas, and mixtures of hydrocarbons with carbon dioxide, based on the reforming reactions of these feedstocks with steam and carbon dioxide and the dehydrogenation reactions of saturated hydrocarbons. Final exit streams from these gas phase processors contain pure hydrogen, hydrogen and carbon monoxide mixture, hydrogen and carbon dioxide mixture, and can be used as a direct feed in molten carbonate, solid oxide, proton exchange membrane, alkaline, phosphoric acid and other types of hydrogen driven fuel cells. Same final exit processed streams can be alternatively used for direct chemical synthesis such as methanol, for hydrogenations and hydrogen based reduction reactions such as those of unsaturated hydrocarbons to paraffins, and as feed in power generation systems such as gas turbines and gas engines.

DRAWINGS (35 U.S.C. 113)

Total sheets : 13

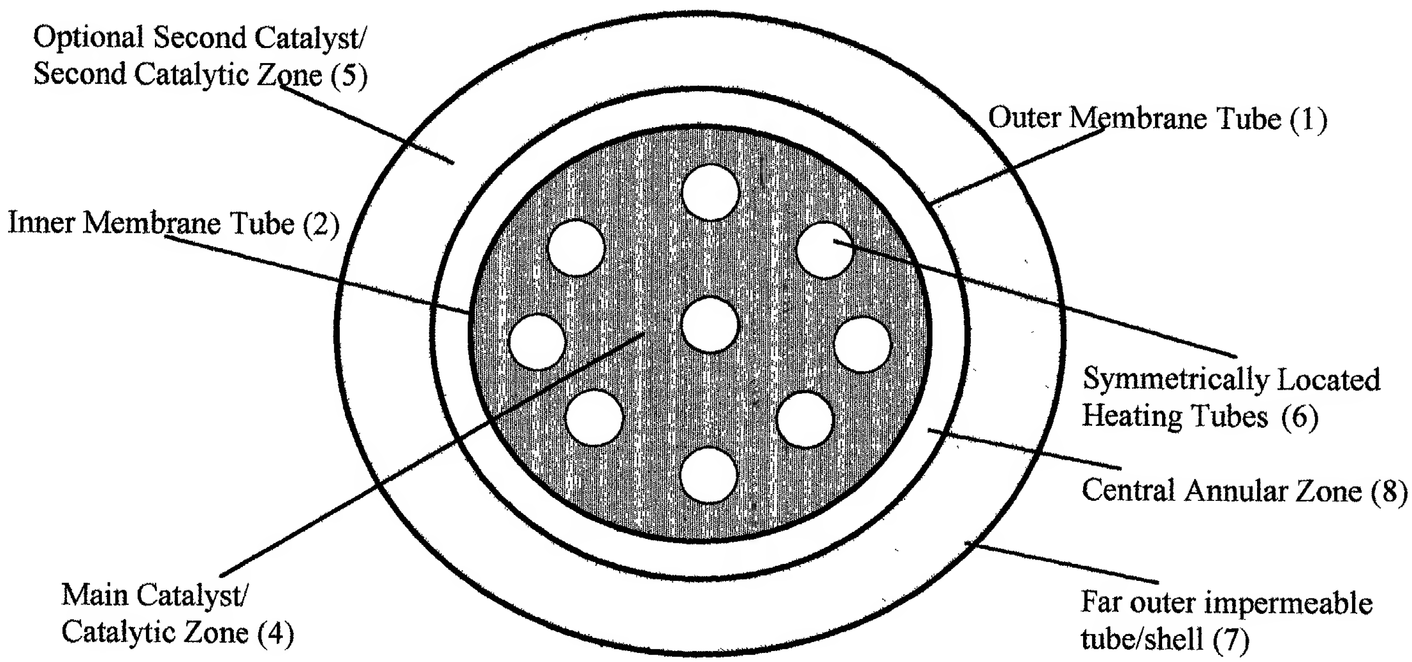

Optional Second Catalyst/
Second Catalytic Zone (5)
Inner Membrane Tube (2)
Main Catalyst/
Catalytic Zone (4)
Outer Membrane Tube (1)
Symmetrically Located
Heating Tubes (6)
Central Annular Zone (8)
Far outer impermeable
tube/shell (7)

**Fig. 1**

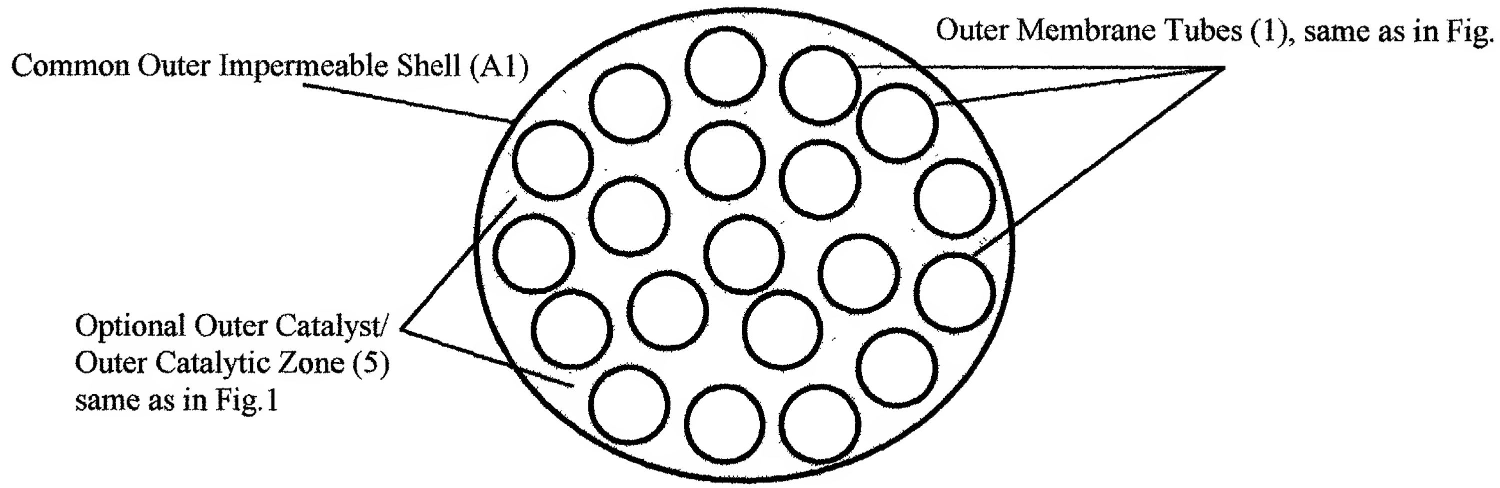

Common Outer Impermeable Shell (A1)
Outer Membrane Tubes (1), same as in Fig.1
Optional Outer Catalyst/
Outer Catalytic Zone (5)
same as in Fig.1

**Fig. 2**

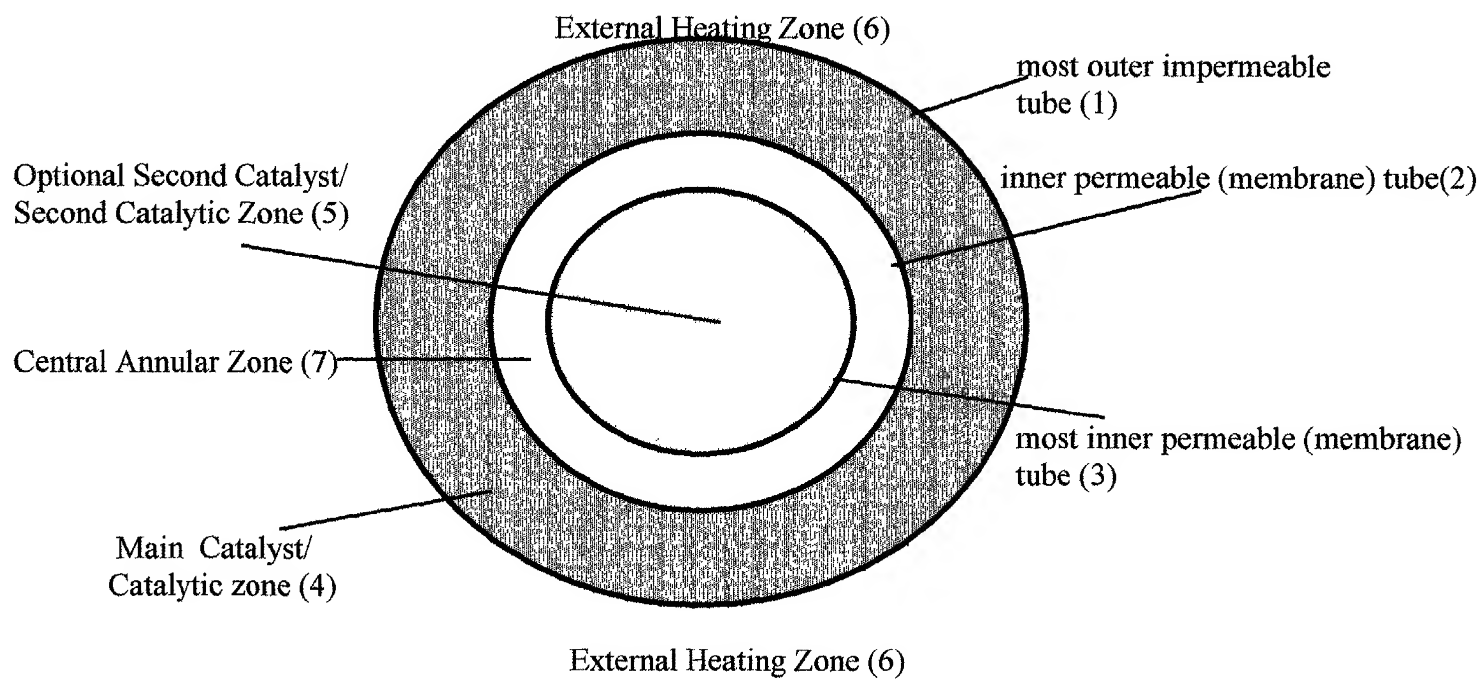

External Heating Zone (6)
most outer impermeable tube (1)
Optional Second Catalyst/ Second Catalytic Zone (5)
inner permeable (membrane) tube(2)
Central Annular Zone (7)
most inner permeable (membrane) tube (3)
Main Catalyst/ Catalytic zone (4)
External Heating Zone (6)

**Fig. 3**

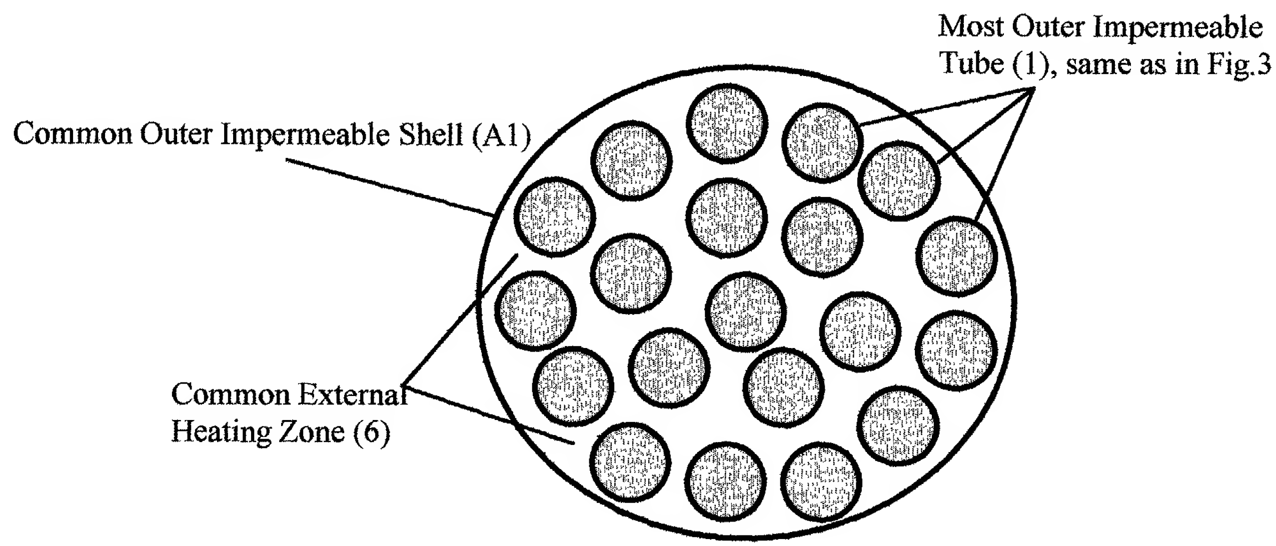

Most Outer Impermeable
Tube (1), same as in Fig.3
Common Outer Impermeable Shell (A1)
Common External
Heating Zone (6)

**Fig. 4**

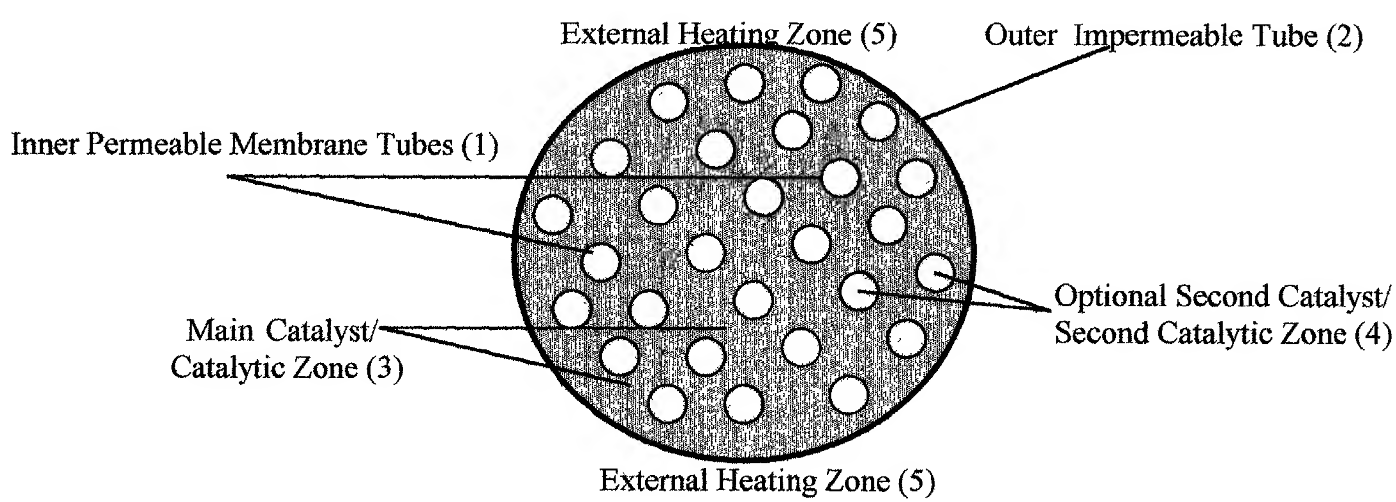

External Heating Zone (5)
Outer Impermeable Tube (2)
Inner Permeable Membrane Tubes (1)
Optional Second Catalyst/
Second Catalytic Zone (4)
Main Catalyst/
Catalytic Zone (3)
External Heating Zone (5)

**Fig. 5**

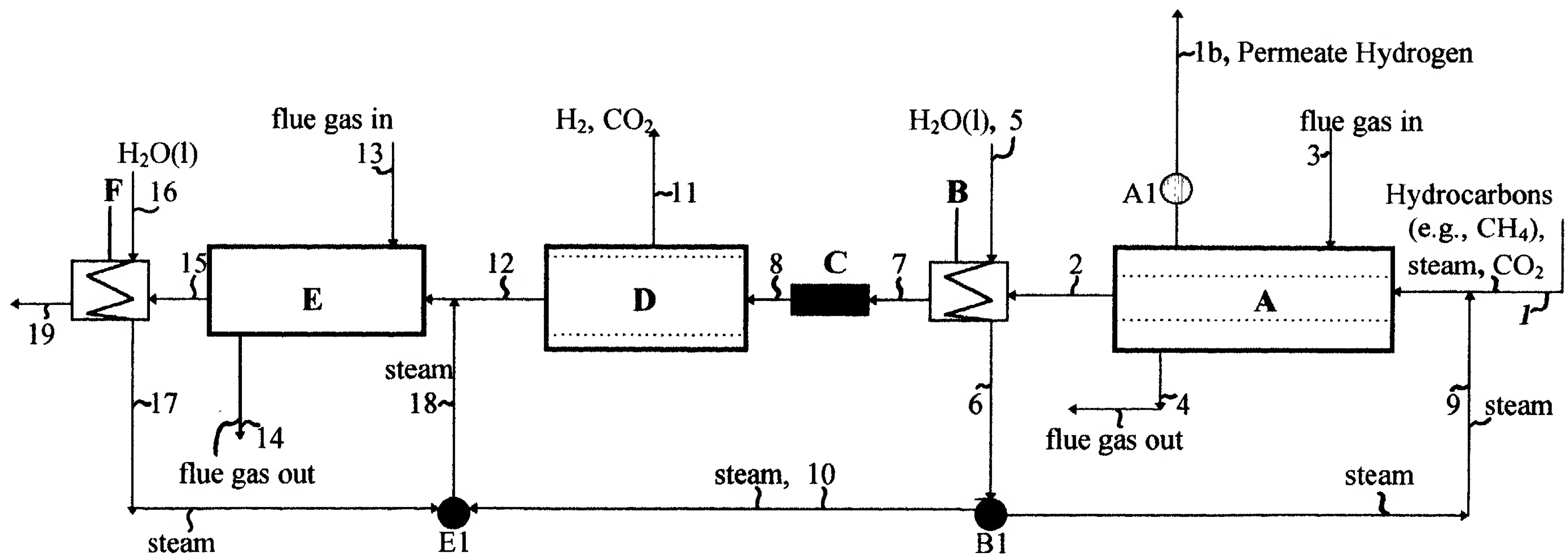
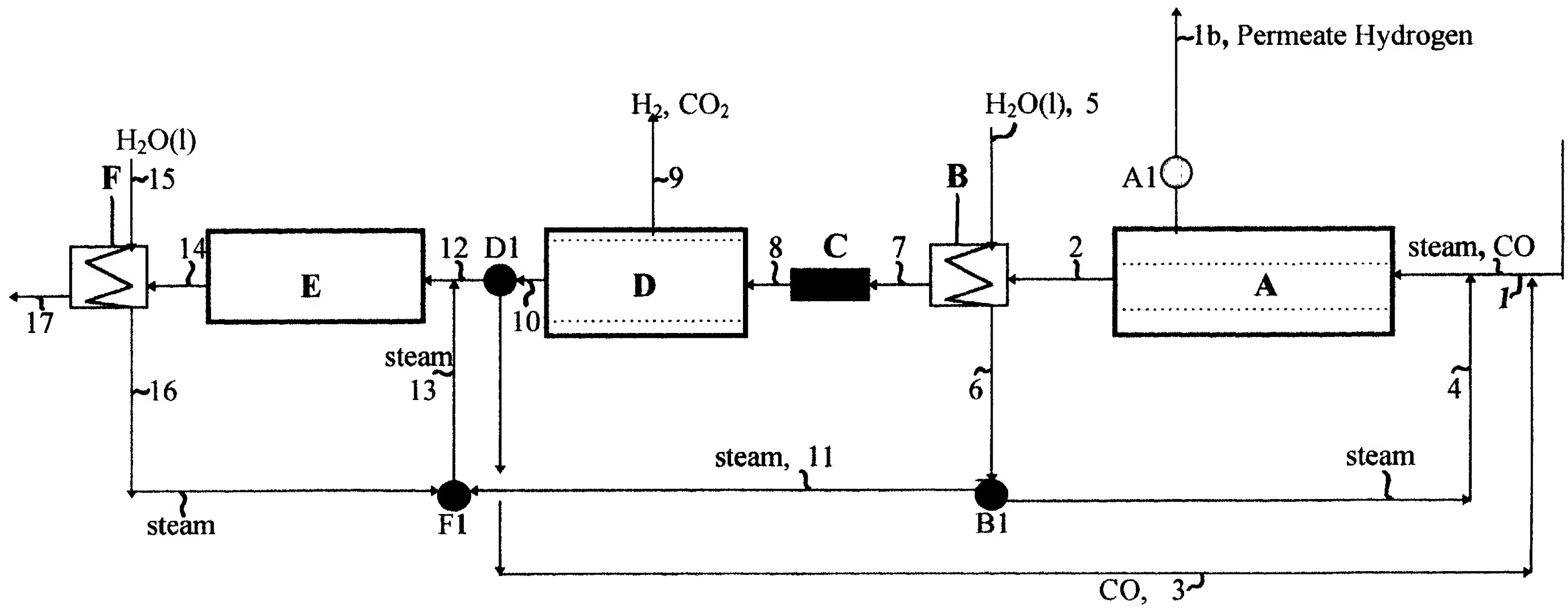

1b, Permeate Hydrogen
flue gas in
H2O(l)
F
16
13
H2, CO2
11
H2O(l), 5
B
A1
3
Hydrocarbons
(e.g., CH4),
steam, CO2
1
15
E
12
D
8
C
7
2
A
19
steam
18
17
14
flue gas out
6
4
flue gas out
9
steam
steam, 10
steam
steam
E1
B1

**Fig. 6**



~1b, Permeate Hydrogen
H2, CO2
H2O(l), 5
H2O(l)
F
~15
~9
B
A1
14
E
12
D1
D
8
C
7
2
A
steam, CO
1
17
10
steam
13
~16
6
4
steam, 11
steam
steam
F1
B1
CO, 3


Fig. 7

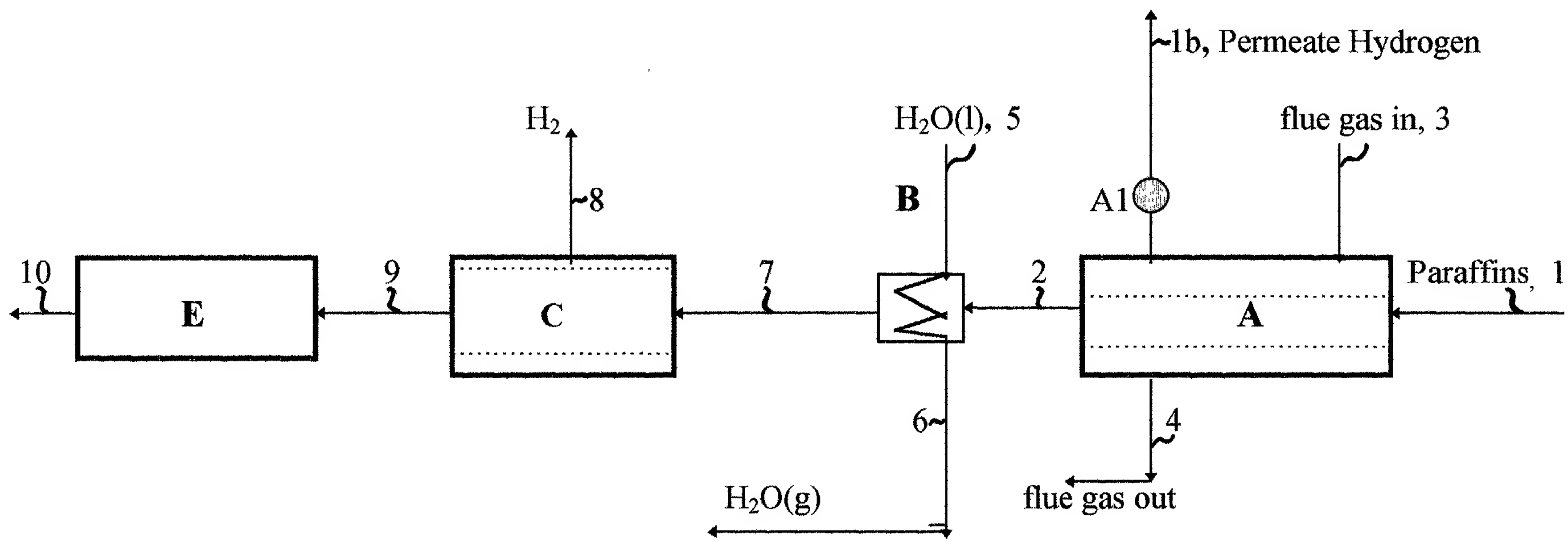

1b, Permeate Hydrogen
flue gas in, 3
$H_2$
8
$H_2O(l)$, 5
B
A1
10
E
9
C
7
2
A
Paraffins, 1
6
4
$H_2O(g)$
flue gas out

**Fig. 8**

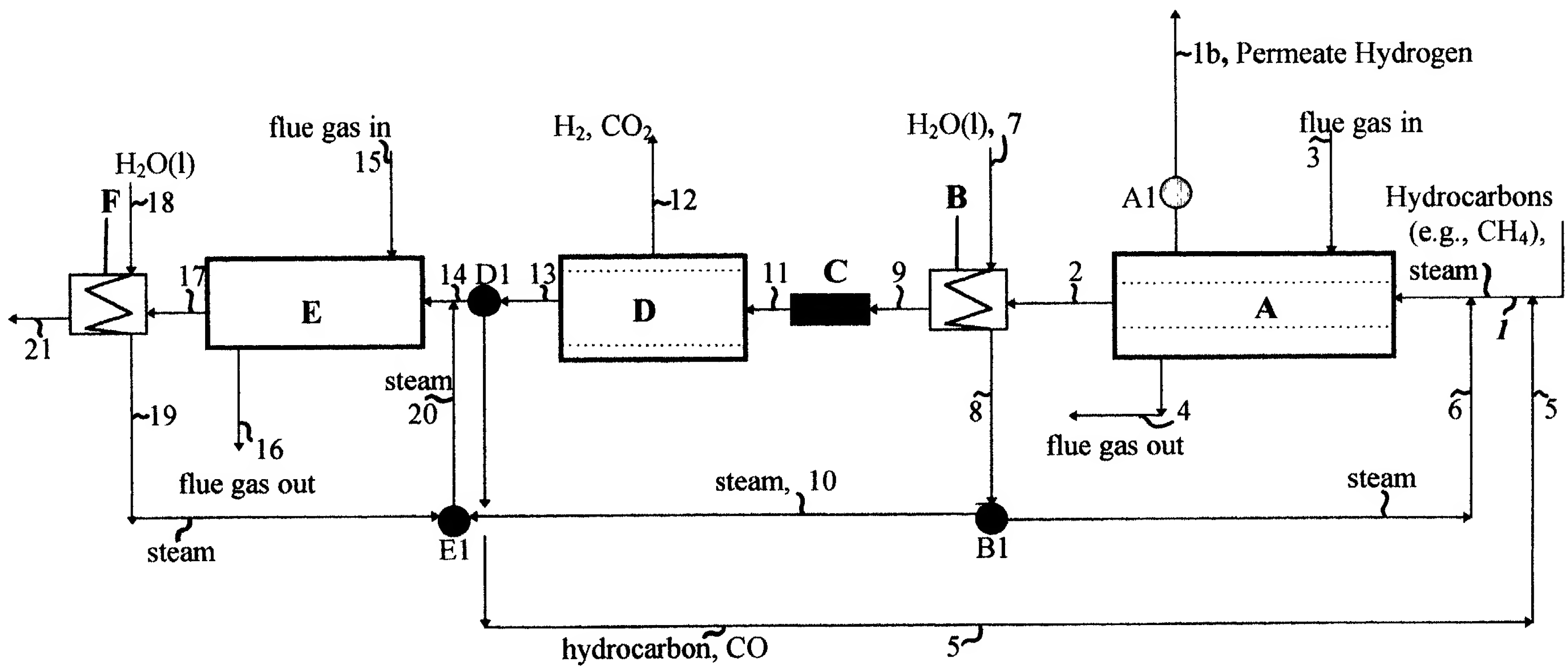

~1b, Permeate Hydrogen
flue gas in
3
Hydrocarbons
(e.g., $CH_4$),
steam
1
A1
A
2
4
flue gas out
6
5
steam
$H_2O$(l), 7
B
9
8
B1
C
11
D
$H_2$, $CO_2$
~12
13
steam, 10
D1
14
E1
steam
20
hydrocarbon, CO
5
flue gas in
15
E
17
16
flue gas out
$H_2O$(l)
F
~18
~19
steam
21

Fig. 9

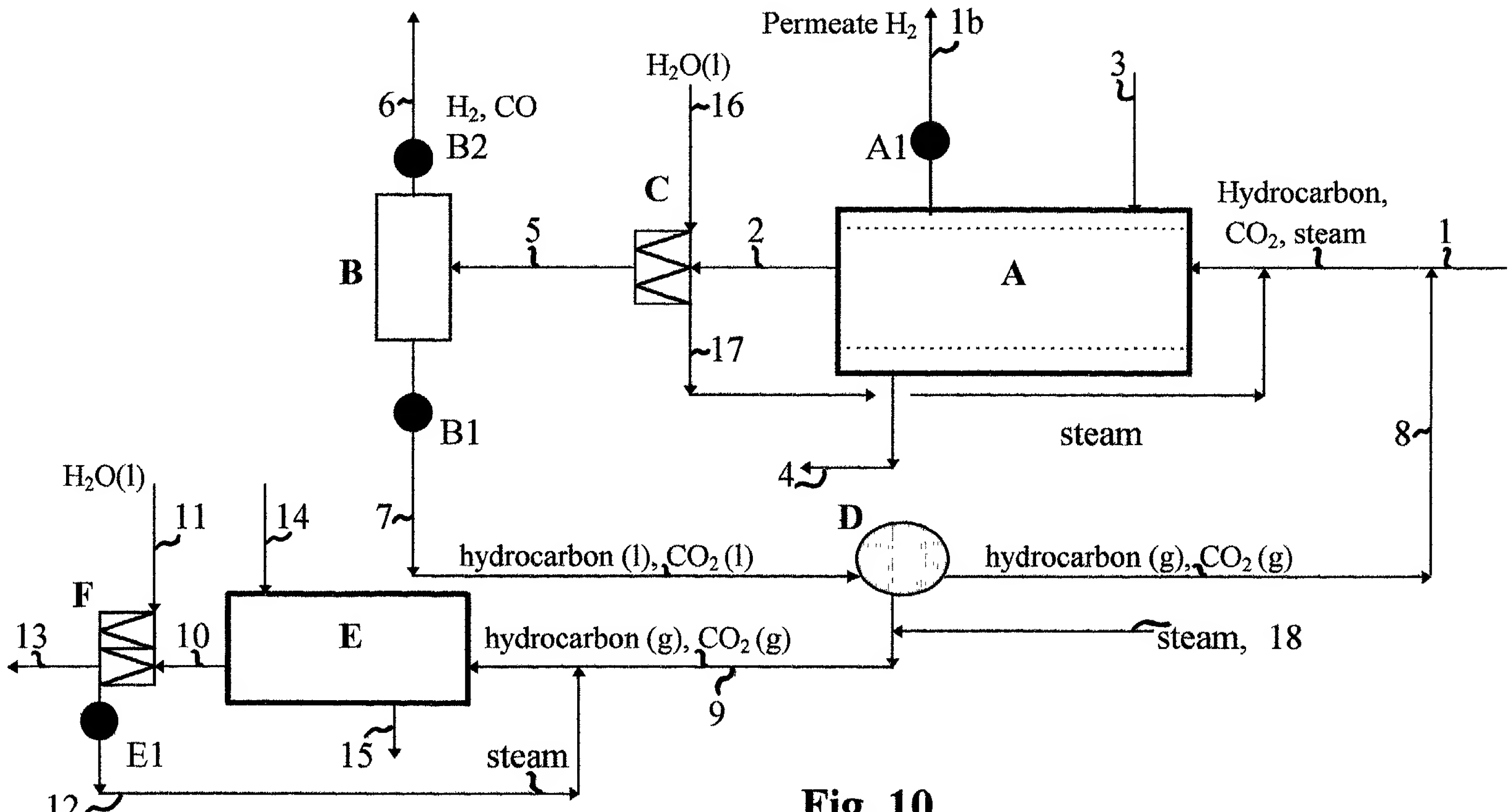

Permeate $H_2$
1b
$H_2O(l)$
16
3
6
$H_2$, CO
B2
A1
C
Hydrocarbon,
$CO_2$, steam
1
5
2
A
B
17
B1
steam
8
4
$H_2O(l)$
11
14
7
D
hydrocarbon (l), $CO_2$ (l)
hydrocarbon (g), $CO_2$ (g)
F
13
10
E
hydrocarbon (g), $CO_2$ (g)
steam, 18
9
E1
15
steam
12

Fig. 10

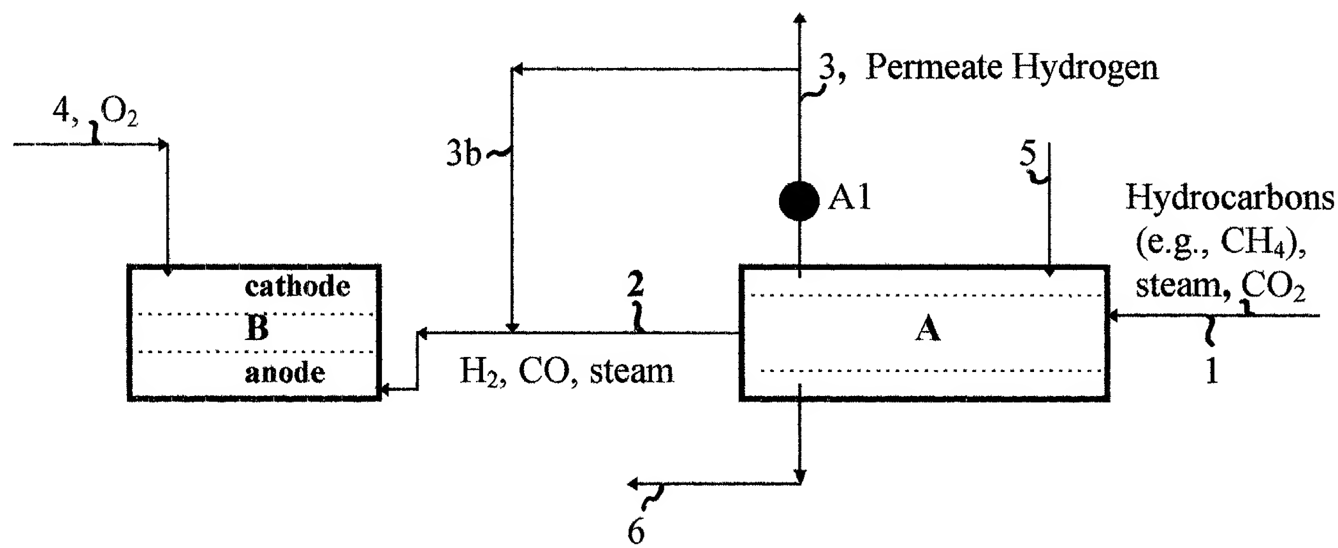
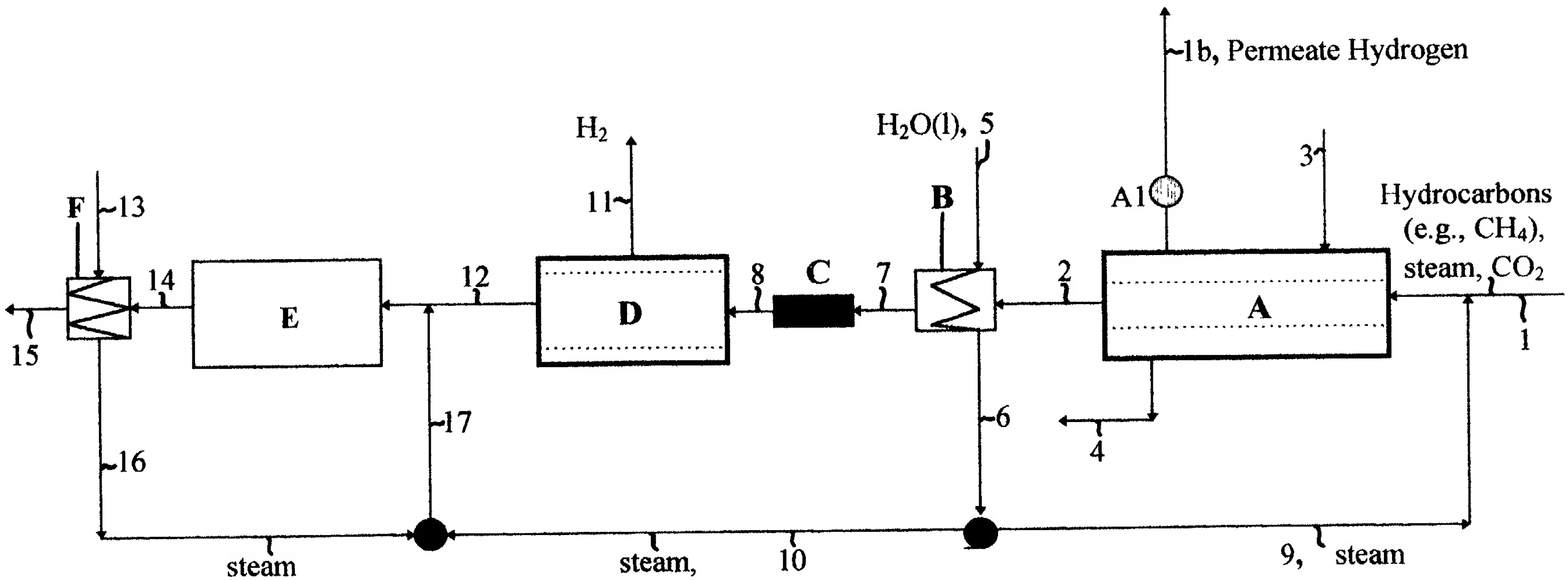
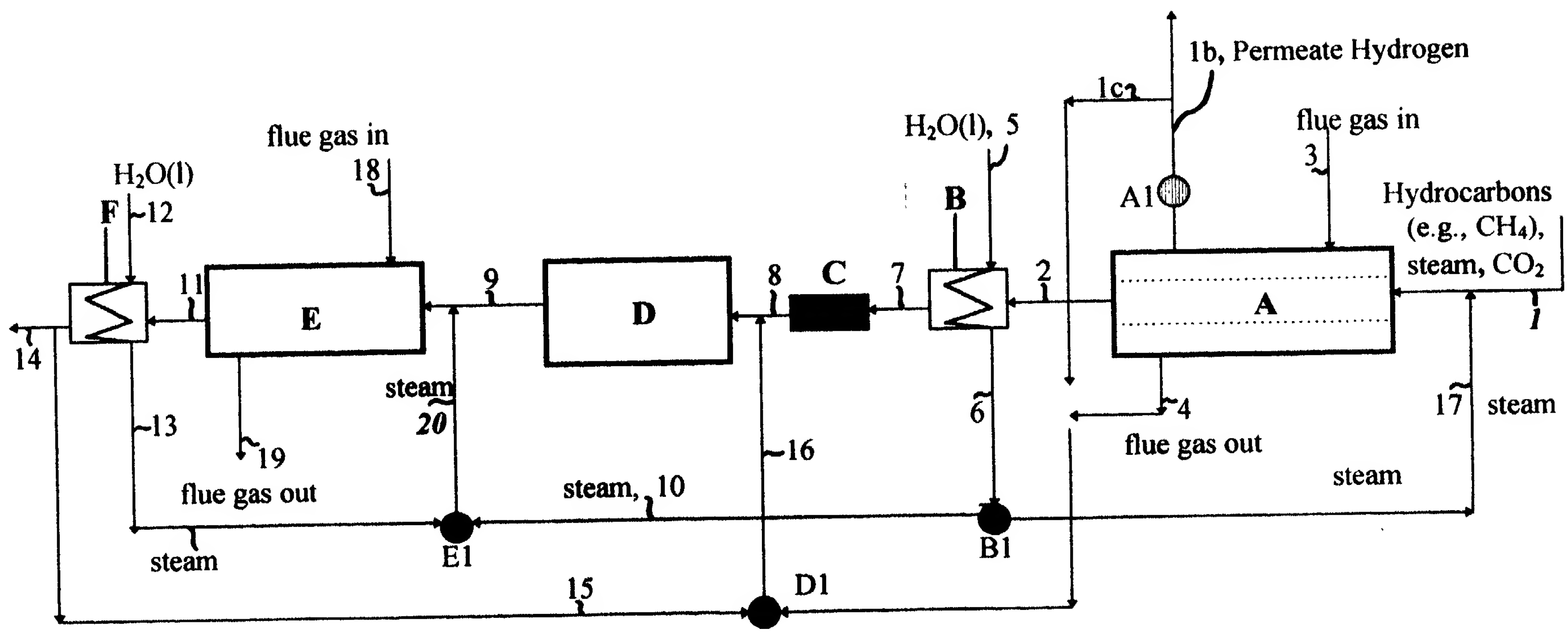

3, Permeate Hydrogen
4, O2
3b
A1
5
Hydrocarbons
(e.g., CH4),
steam, CO2
cathode
B
anode
2
A
H2, CO, steam
1
6

Fig. 11



1b, Permeate Hydrogen
$H_2$
$H_2O(l)$, 5
3
A1
B
F
13
11
Hydrocarbons
(e.g., $CH_4$),
steam, $CO_2$
14
12
8
C
7
2
E
D
A
1
15
17
16
6
4
steam
steam,
10
9,
steam


**Fig. 12**



1b, Permeate Hydrogen
1c
flue gas in
3
Hydrocarbons
(e.g., $CH_4$),
steam, $CO_2$
1
A1
A
4
flue gas out
17
steam
steam
$H_2O(l)$, 5
B
2
6
B1
7
C
8
D
9
16
D1
steam, 10
15
flue gas in
18
E
11
steam
20
E1
19
flue gas out
$H_2O(l)$
F
12
13
steam
14


Fig. 13

Please type a plus sign (+) inside this box → [+]

PTO/SB/02A (3-97)
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| **DECLARATION** | **ADDITIONAL INVENTOR(S) Supplemental Sheet** Page 1 of 2 |
|---|---|

**Name of Additional Joint Inventor, if any:** ☐ A petition has been filed for this unsigned inventor

| Given Name (first and middle [if any]) | Family Name or Surname |
|---|---|
| Savvas | Vasileiadis |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Inventor's Signature | Vasileiadis | | | | | Date | 3/7/2000 |
| Residence: City | North Hills | State | CA | Country | USA | Citizenship | Greek |
| Post Office Address | 15549 Dearborn street, North Hills, CA 91343-3267 | | | | | | |
| Post Office Address | | | | | | | |
| City | North Hills | State | CA | ZIP | 91343-3267 | Country | USA |

**Name of Additional Joint Inventor, if any:** ☐ A petition has been filed for this unsigned inventor

| Given Name (first and middle [if any]) | Family Name or Surname |
|---|---|
| Zoe | Ziaka-Vasileiadou |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Inventor's Signature | | | | | | Date | 3/7/2000 |
| Residence: City | North Hills | State | CA | Country | USA | Citizenship | USA |
| Post Office Address | 15549 Dearborn Street, North Hills, CA 91343-3267 | | | | | | |
| Post Office Address | | | | | | | |
| City | North Hills | State | CA | ZIP | 91343-3267 | Country | USA |

**Name of Additional Joint Inventor, if any:** ☐ A petition has been filed for this unsigned inventor

| Given Name (first and middle [if any]) | Family Name or Surname |
|---|---|
| | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Inventor's Signature | | | | | | Date | |
| Residence: City | | State | | Country | | Citizenship | |
| Post Office Address | | | | | | | |
| Post Office Address | | | | | | | |
| City | | State | | ZIP | | Country | |

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# DECLARATION — Supplemental Priority Data Sheet

Additional foreign applications:

| Prior Foreign Application Number(s) | Country | Foreign Filing Date (MM/DD/YYYY) | Priority Not Claimed | Certified Copy Attached? YES | NO |
|---|---|---|---|---|---|
| | | | ☐ | ☐ | ☐ |
| | | | ☐ | ☐ | ☐ |
| | | | ☐ | ☐ | ☐ |
| | | | ☐ | ☐ | ☐ |
| | | | ☐ | ☐ | ☐ |
| | | | ☐ | ☐ | ☐ |
| | | | ☐ | ☐ | ☐ |
| | | | ☐ | ☐ | ☐ |
| | | | ☐ | ☐ | ☐ |
| | | | ☐ | ☐ | ☐ |
| | | | ☐ | ☐ | ☐ |
| | | | ☐ | ☐ | ☐ |
| | | | ☐ | ☐ | ☐ |
| | | | ☐ | ☐ | ☐ |
| | | | ☐ | ☐ | ☐ |

Additional provisional applications:

| Application Number | Filing Date (MM/DD/YYYY) |
|---|---|
| 08/595,040 | 01/31/1996 |

Additional U.S. applications:

| U.S. Parent Application Number | PCT Parent Number | Parent Filing Date (MM/DD/YYYY) | Parent Patent Number *(if applicable)* |
|---|---|---|---|
| | | | |

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